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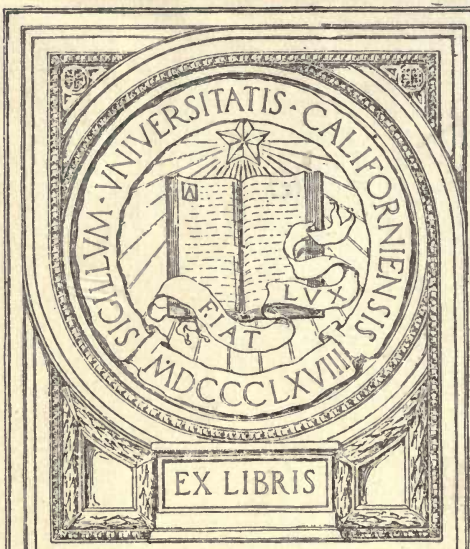
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MOLECULAR DIFFRACTION OF LIGHT

MOLECULAR DIFFRACTION

OF

LIGHT

BY

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To

SIR ASUTOSH MOOKERJEE

with

the author's warmest admiration and esteem.

518434

PREFACE

The fundamental importance of the subject of molecular diffraction came first to be recognized through the theoretical work of the late Lord Rayleigh on the blue light of the sky, which he showed to be the result of the scattering of sunlight by the gases of the atmosphere. It is proposed in this small volume to review the present position of the subject and to discuss the general theory of the molecular scattering of light in all refractive media, including in a comprehensive survey the case of gases, vapours, liquids, crystals and amorphous solids. Experimental observations in support of the theory are detailed, and reference is made to various phenomena in which molecular diffraction plays a part. The case of moving media is also briefly dealt with.

In the course of the work, references are made to cases in which the classical wave-theory apparently fails to explain the facts relating to molecular scattering in a satisfactory manner, and in the final chapter an attempt is made to consider these cases in terms of the conception introduced by Einstein in 1905 that light is not continuous wave-motion but consists of discrete quanta moving through space.

In the writing up of this essay, I have been greatly assisted by the researchers working in my laboratory, references to whom will be found in the pages below. To these gentlemen, I wish to express my heartiest thanks. I am specially indebted to Mr. K. R. Ramanathan M.A., Madras University Research Scholar, for very valuable help in the preparation of the volume and in the carrying out of the experimental work. I am also under great obligations to Sir Asutosh Mookerjee, Vice-Chancellor of the University, for the co-operation which made the publication of the volume possible.

I desire also to record my indebtedness to Mr. A. C. Ghatak, B.A., Superintendent of the University Press and his staff for the quick and efficient manner in which the volume has been printed and got up.

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C. V. RAMAN

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MOLECULAR DIFFRACTION OF LIGHT

CHAPTER I

Fundamental Principles

1. The whole edifice of modern physics is built up on the fundamental hypothesis of the atomic or molecular constitution of matter. In common with other branches of the science, physical optics has to concern itself intimately with the attributes of these molecules or atoms under different conditions and in different states of aggregation and the manner in which they determine the observed properties of substances. The propagation of light through refractive media is in a special degree related to and determined by the molecular structure of these media. The question is, does any departure from perfect regularity of the light-propagation arise from the discontinuous structure of the medium? The

answer to this question forms the subject of the present essay. Under the description of the Molecular Diffraction of Light, we may include such deviations from simple wave-propagation as can be attributed to the ultimate structure of matter.

Rayleigh's Theory

2. The principles on which the problem of molecular diffraction may be handled, at least in the case of gaseous media, were first indicated by the late Lord Rayleigh in one of his well-known papers on the origin of the blue of the sky.[1] Reduced to its essentials, as has been done by Schuster,[2] the treatment is on the following lines. The individual molecules in a gas through which the primary waves of light pass are regarded as secondary sources of radiation, each molecule acting more or less as it would in the absence of its neighbours. There is of course a definite phase-relation between the primary wave when it reaches a given molecule and the secondary wave emitted from it. *In the direction of propagation of the primary waves*, the secondary radiations emitted by all the molecules in a given layer are in identical phase, for, the differences in the phase of the primary wave

[1] Philosophical Magazine, XLVII. 1899, pp. 375-384, Scientific Papers, Vol. IV, p. 397.

[2] Theory of Optics, 2nd edition, p. 325.

when it reaches different molecules are exactly compensated by the acceleration or retardation due to the scattered waves having to traverse a shorter or greater path, as the case may be. *In other directions*, however, owing to the molecules being distributed at random within the volume of the gas, the phases of the scattered waves do not stand in any invariable relation to each other, and hence, in order to find the average expectation of intensity of the scattered light emerging from within the gas, the *intensities*, not the amplitudes, of the waves scattered by the individual molecules should be added up. In all ordinary cases, there is very little difference of phase between the primary wave reaching an individual molecule and the secondary wave sent out by it so far as the direction of original propagation of the wave is concerned. When, however, the effect of all the molecules contained in a stratum parallel to the plane of the primary wave is integrated by the usual method of sub-division of the stratum into Fresnel zones, and the resultant is combined with the primary wave, a change of phase appears which may be identified as the retardation associated with the passage of waves through a refractive medium. A relation is thus obtained between the scattering power of the molecules, their number per unit volume and the refractivity of the medium. Thus, taking the light vector in the primary waves to be

represented by $R_o \cos(\omega t - lx)$ where x is measured from the position of the scattering molecule, the vector in the scattered wave arising from it may be written as

$$A_1 \cos(\omega t - lr). \quad R_o \sin\theta/r \ldots\ldots\ldots\ldots (1).$$

when r is the distance from the molecule and θ is the angle between the vibration at the origin and the scattered ray. On carrying out the calculations indicated, the relation obtained is

$$N A_1^2 = \frac{4\pi^2(\mu-1)^2}{N\lambda^4} \quad \ldots\ldots\ldots\ldots (2).$$

where N is the number of molecules in unit volume, λ is the wave-length of the light and μ is the refractive index of the gas.

3. The energy scattered by the molecules in the interior of the gas must be derived from the primary beam, and hence the intensity of the latter must suffer an attenuation as it passes through the medium. The coefficient of attenuation may be readily evaluated by a simple calculation of the total energy scattered by an individual molecule and then multiplying this by the number N of molecules per unit volume. We thus obtain the intensity of the transmitted light to be $I = I_o e^{-\kappa x}$ where κ the coefficient of attenuation is given by the relation

$$\kappa = \frac{32\pi^3(\mu-1)^2}{3N\lambda^4} \quad \ldots\ldots\ldots\ldots (3).$$

This expression for the attenuation coefficient may also be derived directly by

a more accurate investigation which does not neglect the small difference of phase between the primary wave and the secondary waves originating at a molecule. It is then found that on compounding the effects of the primary wave with those of the secondary waves arising from a stratum of molecules, there appears in addition to the alteration of phase of the primary wave, also a small diminution in its intensity which is exactly that expected in view of the lateral scattering of part of the energy.

Criticisms of the Theory

4. In connection with the treatment outlined above, two distinct points come up for remark. According to Lord Rayleigh's treatment, $(\mu-1)$ is proportional to the number of particles per unit volume of the gas, in other words varies directly as the density when the pressure is increased. In other words, the theory leads to Gladstone and Dale's law for the relation between refractive index and the density. It is well-known however that this law is only an approximation, a more accurate relation between the refractive index μ and the density ρ being the Lorentz-Mossoti formula

$$\frac{\mu^2-1}{\mu^2+2} = \text{constant.}\ \rho \qquad \ldots\ldots\ldots\ldots(4).$$

The derivation of this formula has been discussed by Rayleigh[1] and it is clear that to be quite strict, the treatment of the problem of molecular diffraction should be modified so that it leads to (4) as the relation connecting the density with the refractive index. It may be mentioned however that in the case of gases at ordinary pressures the error involved in overlooking this point would not be appreciable.

5. A more important question is the justification for the view that the phases of the waves laterally scattered by the individual molecules are absolutely at random, so that their energy-effects are additive. In the earlier treatment given by Lord Rayleigh, this was by no means made entirely clear, and on a superficial view of the matter it might be questioned (as indeed it has been by Sir Joseph Larmor)[2] whether the phase relation of the scattered waves arising from the molecules in any small volume is indeed in reality subject to such large and arbitrary variations that the energies due to the individual molecules may be summed up without any sensible error from their mutual interference. Larmor points out that in the

[1] Philosophical Magazine, Vol. XXXIV, pp. 481-502, 1892, Scientific Papers, Vol. IV, p. 19.

[2] Phil. Mag., Jan. 1919, p. 161. These comments of Larmor were made with reference to a paper by Rayleigh in the Phil. Mag. for Dec. 1918, dealing with the general problem of the light emitted from a random distribution of luminous sources.

case of a gas at atmospheric pressure, there are 10^6 molecules in a cubic wave-length so that the scattered waves arising from adjacent molecules differ in phase by only 10^{-2} of the period and asks, in view of this closeness of packing of the molecules whether, if they could be regarded as fixed while the radiation was passing, they ought not in conjunction to scatter far less than they would do separately? The difficulty will perhaps appear even more acutely if we consider a gas at fairly high pressure, say 64 atmospheres. The average difference of phase for adjacent molecules is in this case only $2{\cdot}5\times10^{-3}$ of a period, and the mean free path of a molecule would be only about $0{\cdot}02\times10^{-5}$ cms., that is, less than $\frac{1}{250}$ of the wave-length of sodium light. Could we in the circumstances consider the phases of the scattered waves arising from individual molecules to be distributed entirely at random?

6. The difficulty referred to in the preceding paragraph appears to have impressed Larmor so greatly that in order to find a way of escape from it, he has suggested a somewhat different logical basis for the empirically observed correctness of the result deduced from Rayleigh's theory. It seems best to quote Larmor's own words: "The molecules of the atmosphere are in thermal motion, with velocities in correlated directions which are at ordinary temperatures

of the order of 10^{-6} of that of the radiation. The wave-length of the radiation scattered from them will thus vary within a range of 10^{-6} of itself. If the phases of the scattered radiations are correlated at first, after traversing 10^6 wave-lengths or 50 cms. they will have become fortuitous, and the energy effects thus additive. This consideration, if justified would find the source of Lord Rayleigh's principle in the uncoordinated thermal motion of the molecules."

Justification of the Principle of Random Phase

7. With regard to the remarks by Larmor quoted above, it may be pointed out that the difficulty raised cannot be evaded in the manner proposed by him. The suggestion made is that the phases of the scattered radiations emerging from the column of gas may be correlated at first but after traversing 10^6 wave-lengths or 50 cms., they would have become fortuitous and the energy-effects thus additive. If this were correct, we should find that the aggregate intensity of the scattered light should be small immediately after emergence from the column of gas, that is when it is observed within a distance of a centimetre or two from the track of the primary

beam, and should increase at a greater distance from it. Such a result is obviously quite inadmissible, besides being contrary to experience. The fallacy lies in the assumption that the change of wave-length (Doppler effect) has an effect on the relative phases of the scattered waves, whereas in reality it has none. To make this clear, we may consider two neighbouring molecules A and B. The scattered waves originating from them travel outwards with an identical velocity which is quite unaffected by any movements of these molecules. The phase-difference at any epoch therefore remains unaffected as the waves move out, being exactly the same as when the portions of the wave-train under consideration left the molecules. In other words, the phase-difference at each stage is exactly the same as if the molecules had remained fixed from the instant of emission of the scattered light. The scattering from any appreciable volume of gas would thus remain unaffected if all the molecules were assumed suddenly to be fixed in their instantaneous positions, and the Doppler effect due to their movement exerts no influence whatever on the observed results. Larmor's suggestion therefore clearly fails.

8. What then is the justification of Rayleigh's principle? The answer to this question becomes plain when we consider the implications contained in the propositions under discussion.

In order that the phases of the scattered waves arising from the individual molecules should be entirely fortuitious, it is clearly necessary and sufficient that the distribution of the molecules in the space enclosed within the walls of the containing vessel should be itself entirely fortuitous. This again in its turn would be true, if the probability that a given molecule is found within a small specified volume is independent of the presence of any other molecules, in other words if the probability that two or more given molecules are found together within a specified space is the product of the probabilities of each of them separately being found within the space. This will be true provided the total volume of the molecules or rather of the spheres of influence within which their mutual action on each other is sensible forms a sufficiently small fraction of the total space occupied by the molecules. This is precisely the condition necessary that the relation between the pressure and volume of a gas should be that given by Boyle's law. In other words, we have a truly random distribution of the molecules provided the compressibility of the gas at the pressure under consideration does not appreciably deviate from that derived from Boyle's law. So long as this is the case, Rayleigh's principle must be substantially valid, and neither the closeness of the packing nor the smallness of the free path of

the molecules in relation to the wave-length of light can influence the result appreciably.

9. A precisely similar result is also arrived at if we investigate the condition necessary that the light scattered by an appreciable proportion of the molecules in the given volume may be extinguished by their mutual interference. It is obvious immediately that if the molecules be distributed *uniformly* throughout the containing vessel, we may divide up the entire volume into a large number of very small equal elements each containing a few molecules, and take them off in pairs situated at such distances from each other that in any specified direction, the scattered waves from the components of each pair differ in phase by π and therefore cut each other out by interference. In such a case, it is clear that there would be no scattered light emerging from within the gas. (A few elements of volume might be left over surplus and uncompensated near the boundaries of the vessel. These would give a surface-effect with which we are not here concerned.) If however we attempt to apply similar reasoning in the case of an actual gas the argument breaks down. The distribution of the molecules is no doubt such that the density of the medium does not vary by any appreciable fraction of itself when we consider any appreciable volume, say one cubic wave-length. But when the sub-division

of the space is carried further, deviations from the equality of the number of molecules present in equal elements of volume become relatively more important, until finally when we consider volume-elements of molecular dimensions the probability that a molecule will be found inside such an element becomes small and in the case of a gas obeying Boyle's law with accuracy, vanishingly small. Thus if we take two volume elements of molecular size at a distance *exactly* $\lambda/2$ apart, the expectation that they would both simultaneously hold molecules whose effects would mutually extinguish one another is vanishingly small. Thus again we see that no appreciable proportion of the energy scattered by the individual molecules is taken off as the result of interference.

10. The foregoing discussion makes two points clear. The validity of the principle of random phase depends on the conditions being such that the compressibility of the medium is given with sufficient accuracy by Boyle's law. Secondly, the ultimate justification of the principle rests on the complete non-uniformity in the spatial distribution of the molecules in so far as very small volume elements are concerned. As we shall see later on, it is precisely these factors, namely, the compressibility of the medium and the non-uniformity of the spatial distribution of the molecules, which enter into

the general theory of light-scattering developed according to the principles laid down by Einstein and Smoluchowski, and which, as has been pointed out by these writers, in the case of *gases* obeying Boyle's law leads to results substantially identical with those obtained from Rayleigh's formula. It is important therefore to notice that in respect of gases at any rate, the special theory developed by Rayleigh and the more general theory of Einstein and Smoluchowski rest on exactly the same logical bases and differ only in the detailed mode of calculation of the intensity of the light scattered.

CHAPTER II

Scattering of light by gases

11. In view of the very satisfactory explanation by Lord Rayleigh and Schuster of the blue of the sky and the observed degree of transparency of the atmosphere on the basis of molecular diffraction, it became obviously a question of great importance to detect, and if possible, to measure, the scattering of light by dust-free air in the laboratory. The first successful attempt in this direction was made by Cabannes.[1] Later work on the experimental side of the subject, including scattering by other gases and vapours, has been done by Prof. R. J. Strutt[2] (the present Lord Rayleigh), by Cabannes[3] himself, by Smoluchowski[4] and by Gans[5].

12. The methods adopted by these investigators are essentially similar. The gas is contained in a cross-tube dead-blacked inside. An intense

[1] Cabannes—Comptes Rendus, CLX, p. 62, 1915.
[2] R. J. Strutt—Proc. Roy. Soc., XCIV, p. 453, 1918.
[3] Cabannes—Ann. de Physique, Tome XV. pp. 1-150.
[4] Smoluchowski—Bulletin De la Academie Cracovie, p. 218, 1918.
[5] R. Gans—Ann. der Physik, 10, 1921.

beam of light is sent along one of the tubes, and the scattered light is observed in a perpendicular direction. Owing to the extreme faintness of the scattered light, the background has to be perfectly black in order that the track of the beam may be visible. The best arrangement to secure this is that adopted by Strutt in his later work. He used as a prolongation of the observation tube a curved horn blown out of green glass and covered outside with black paint. The object of the glass horn is to reflect any stray light that falls on its mouth repeatedly towards the narrow end and thus to absorb it. With such a background the track of a beam of sunlight concentrated by a lens in dust-free air is easily visible. Of course, the gas under observation has to be carefully freed from dust before introduction to the chamber by *slow* filtering through a tube tightly packed with cotton wool, and in the case of gases attacked by light, care has to be taken to exclude rays having any chemical action.

Intensity and Polarisation of the Scattered Light

13. According to Lord Rayleigh's calculation, the intensity of the light scattered by one cubic centimetre of a gas having symmetrical molecules in a direction perpendicular to the incident

beam should be proportional to $(\mu-1)^2$.[1] The experiments of Strutt led him to the conclusion that this was so, within the limits of experimental error. The following table gives his results :—

Gas.	Scattered light.	Refractivity.[2]
Air (assumed)	1·00	1·00
Hydrogen	0·230	0·229
Nitrous Oxide	3·40	3·12
Ether vapour	26·0	27·1

The careful experiments of Cabannes,[1] showed however, that although the law was true in its main features, there were differences in the value of the observed scattering from the calculated values too large to be explained as being due to experimental error.

14. On the assumption of symmetrical molecules, the light scattered in a direction perpendicular to the incident beam should be completely polarized with the electric vector perpendicular to the plane containing the incident and scattered beams. Strutt examined the polarisation of the scattered beam and obtained for the first time the remarkable result that, in many gases, the scattered light is only partially polarised.

[1] Cabannes (loc. cit.) has calculated the scattering co-efficient on the basis of the electromagnetic theory and obtains a value $\frac{\pi^2}{2n\lambda^4}\cdot(\mu^2-1)^2$. When $(\mu-1)$ is small, this reduces to $\frac{2\pi^2}{n\lambda^4}(\mu-1)^2$, (See also Schuster Proc. Roy. Soc., XCVIII, p. 248.)

The experimental method adopted by Strutt for the examination of polarisation was to place a double image prism with its principal section perpendicular to the incident beam in the path of the scattered light and obtain an image of the luminous track on a photographic plate. Two images were in general obtained, a strong one with the electric vector in the direction indicated by the ordinary theory and a weak one with the electric vector in the perpendicular direction. The two images could be made of equal intensity by inserting a nicol between the double image prism and the camera and properly orienting the nicol, and from the known angle between the principal planes of the nicol and double image prism, the ratio of the weak component to the strong could be calculated.[1]

15. The imperfect polarisation of the light scattered by gases has also been observed *visually* and measured in experiments undertaken at the author's suggestion by Mr. K. R. Ramanathan at Calcutta. For this purpose, an apparatus was used similar to that of Lord Rayleigh and the gas was illuminated by means of a concentrated beam of sunlight, great care being taken to shield the observer's eye from extraneous light. With air at ordinary pressure, the intensity is not sufficient

[1] In his earlier work, Strutt used a series of graded blackened photographic plates in the path of the stronger component so as to get the intensities of the two components equal.

to make more than a rough photometric estimate feasible, but when we use carbon dioxide which scatters nearly three times as much light as air, fairly accurate measurements are possible by visual observation. Such a comparison leads to a value 10% for the ratio of the weak to the strong components as against 9·9% obtained by Cabannes and 11·7% obtained by Strutt. More accurate measurements can be made visually with the gases at higher pressure and an apparatus is nearly ready for the purpose.

16. I give below for comparison the values of the ratios of the weak component to the strong for different gases obtained by Strutt and Cabannes. The figures give the weak component as a percentage of the strong component.

Gas.	Strutt.	Cabannes.
H_6	3·83	Between 1 and 2
N_2	4·06	„ 2·5 and 2·8
Air	5·0	„ 3·7 and 4·0
O_2	9·4	„ 5·1 and 5·4
CO_2	11·7	„ 9·5 and 9·9
Argon	<0·5	<0·8
He	<6.5	

Strutt estimates the error of his results to be not more than 5% . In view of the great care that Cabannes also seems to have bestowed on his work, it is remarkable that Strutt's results should be systematically higher than those of

Cabannes.[1] One reason that suggests itself for this systematic difference is the difference in the quality of the light employed by the two experimenters. Strutt used a carbon arc, while Cabannes used a mercury arc, the active radiations being 4358, 4046 and 3650 A.U., the rest of the radiations being filtered out. Since both the experimenters used the photographic method, it is the violet and ultraviolet that would have been most effective. Considering the very great intensity of the carbon arc in the region of 3000-4000 A.U. it is possible that the effective wave-length in the case of Strutt's experiments was smaller than in those of Cabannes. The question of the influence of wave-length on the ratio of the components in the imperfect polarisation of the scattered light is one of great importance, and is being examined experimentally by Mr. Ramanathan at the author's laboratory.

Explanation of Imperfect Polarisation.

17. The imperfect polarisation of the scattered light has been explained on the basis of a suggestion made tentatively in a much earlier paper by the late Lord Rayleigh[2] that the molecules have three principal axes of symmetry and that they are oriented at random.

[1] In his earlier work, Strutt got results which are in better agreement with those of Cabannes.

[2] Phil. Mag., Vol. XXXV, pp. 373-381, May 1918.

His method consists in resolving the primary vibrations along three mutually perpendicular directions in the molecule and introducing separate co-efficients of radiation for the different axes and integrating the effect due to a large number of molecules in all possible orientations. He obtains for the ratio of the weak component to the strong in the scattered radiation the value

$$\frac{i}{I} = \rho = \frac{A^2+B^2+C^2-AB-BC-CA}{3(A^2+B^2+C^2)+2(AB+BC+CA)}$$

where A, B, C are three parameters characteristic of the molecule and to some extent, dependent on the frequency of the incident light. Taking the imperfection of polarisation into account, Cabannes has shown that the intensity of the scattered light is not given by the formula

$$\frac{\pi^2}{2}(\mu^2-1)^2\,\frac{1}{N\lambda^4}, \text{ but by } 3\pi^2\,\frac{(\mu^2-1)^2}{N\lambda^4}\,\frac{1+\rho}{6-7\rho}$$

Since ρ differs for different gases, the intensity of the scattered light would not be proportional to the square of the refractivity, but to

$$(\mu-1)^2\,\frac{1+\rho}{6-7\rho}$$

18. The following table shows the nature of the agreement between the observed [1] and calculated values according to Cabannes:—

Ratio of Intensities of Scattered Light.

	Observed	$\frac{(\mu_1-1)^2}{(\mu_2-1)^2}$	$\frac{(\mu_1-1)^2 \frac{1+\rho_1}{6-7\rho_1}}{(\mu_2-1)^2 \frac{1+\rho_2}{6-7\rho_2}}$
$\frac{\text{Argon}}{N_2}$	0·829	0·90	0·823
$\frac{Co_2}{\text{Argon}}$	3·31	2·53	3·12
$\frac{Co_2}{\text{Air}}$	2·62	2·35	2·65
$\frac{Co_2}{O_2}$	2·93	2·80	3·07
$\frac{H_2}{O_2}$	0·255	0·276	0·255

19. Sir J. J. Thomson[2] has calculated the ratio of the weak to the strong component in the light scattered at different angles with simple molecular models for the hydrogen molecule and comes to the conclusion that, with two positive charges at A and B and two electrons rotating in a circle at the opposite ends of a diameter in a plane bisecting AB at right angles, the ratio of the minimum to the maximum intensity of the components of the scattered

[1] Cabannes, pp. 1-150, Ann. de Phys., 1920.

[2] Phil. Mag, 393, XL, 1920.

light would only be 0·4 per cent. while the actual experimental value is nearly 4 per cent. But with two electrons kept in equilibrium by a modified inverse square law, a value for the ratio nearly the same as the experimental ratio is obtained. His calculations indicate that although the polarisation is imperfect in a direction perpendicular to the incident beam, it may be perfect in a different direction. Experimental work on the intensity of scattering and polarisation in other than transverse directions might therefore prove of interest. Born [1] and later, Born and Gerlach,[2] have tried to calculate the scattering on the basis of the Bohr-Sommerfeld models of the molecules. Their results also indicate a dependence of the imperfection of polarisation on the frequency of the incident light, the imperfection increasing as the natural frequency of the molecule is approached. The values which Born obtains for the imperfection of polarisation do not however agree with the experimental results. The position appears to be, therefore, that models based on the quantum theory have not yet succeeded in solving the problem of molecular scattering.

20. It is also pretty certain that Rayleigh's law must break down when the frequency of

[1] Ver. Deutsch. Phys. Gesellsch. 16, 1918.

[2] Zeit. fur. Physik. 374, 1921.

the incident light is sufficiently increased. The phenomenon of resonance radiation is sufficient proof of the fact. The transition from ordinary scattering to resonance would be very interesting to study, although the subject is beset with considerable experimental difficulties. It would also be of interest to study by the scattering absorbing gases like chlorine on either side of the region of absorption.

CHAPTER III

Atmospheric Scattering and Twilight Phenomena

21. Following upon the publication by the late Lord Rayleigh of his brilliant idea that the scattering of light by the molecules of air accounted in large measure both for the blue light of the sky and the observed degree of transparency of the atmosphere, the subject was taken up by Lord Kelvin[1] and by Prof. Schuster[2] and it was shown that the suggestion was in quantitative agreement with the facts. The subsequent development has been largely a matter of detail and owes its interest to the importance of the problem from the standpoint of solar and terrestrial meteorology rather than that of theoretical physics. Among the principal contributions subsequent to the pioneer investigations referred to above may be mentioned especially the work of Abbot and Fowle[3] and the theoretical researches of Prof. L. V.

[1] Baltimore Lectures, 1904, pp. 301-322.

[2] Treatise on Optics, 2nd edition, p. 329.

[3] Annals of the Astrophysical Observatory, Vol. II, and Astrophysical Journal, 38, 1913.

King[1] in which an attempt is made to take secondary scattering into account and to discuss the disturbing effects produced by atmospheric "dust." A large amount of detailed work, chiefly of an observational kind on the character and intensity of sky-radiation and on atmospheric absorption has also been published. The main result has been the confirmation of Rayleigh's theory, but nothing essential has been added to it except perhaps the recognition of the importance of taking into account the selective absorption in certain regions of the spectrum exercised by the gases of the atmosphere and by the water-vapour present in it.

22. The newer work of Cabannes and of the present Lord Rayleigh in their laboratory experiments on molecular scattering by gases and the subsequent theoretical discussions of their results have however opened up novel issues. Two new facts have emerged, namely, the imperfect polarisation of the transversely diffracted light, and the influence of this imperfect polarisation on the intensity of the scattered light. A third point is also suggested by theory that the magnitude of the imperfect polarisation may depend to an appreciable extent on the wavelength of the incident light. It is natural to ask the question, is there any evidence of

[1] Philosophical Transactions of the Royal Society, A 212, 1913.

these effects to be found in the observations on sky-radiation? Then again, a perusal of the literature shows that several interesting problems relating to molecular diffraction in the atmosphere have not as yet been the subject of mathematical treatment. Notable amongst these is the explanation of twilight phenomena regarding which very little theoretical work has been done. It is proposed in this chapter briefly to review the outstanding problems relating to atmospheric scattering which are of interest from the standpoint of theoretical physics and to indicate the lines of advance.

The Polarisation of Skylight.

23. As mentioned above, the first novel issue which is raised by the newer work is the extent of polarisation of molecularly diffracted light. As is well-known, the light of the sky observed in a direction 90° remote from the sun is strongly but not completely polarised, the degree of such polarisation depending not only on the wavelength of the light under consideration but also to a large extent upon the altitude of the sun, the meteorological condition of the atmosphere and other factors. The defect of polarisation under ordinary conditions is in fact so considerable that not more than a small fraction of it, if at all, is that inherent in molecular diffraction.

Much the larger part arises from disturbing factors, such as dust, thin clouds or haze, secondary scattering due to the self-illumination of the atmosphere and light reflected from the earth's surface. We may ask, is it at all possible to eliminate these factors altogether or to disentangle their effects and establish the imperfect polarisation to molecular anisotropy by observations of skylight? At first sight this may seem very difficult, but a little consideration will show that the attempt is not quite so hopeless as may be thought. As is well-known, dust and haze are largely confined to the lower levels of the atmosphere. This is beautifully illustrated by the aeroplane photographs secured by Luckiesh[1] which show a well-marked dust or haze horizon lying at an altitude of about a mile above the earth' s surface. Mr. Evershed has mentioned to the author in conversation that from the observatory at Kodaikanal which is above the dust-level, its rise and fall with the change of seasons can be seen against the dark back ground provided by a distant mountain. It is clear therefore that by making the observations on a high mountain on a bright clear day, it should be possible practically to eliminate the effect of dust and haze on the polarisation of sky-light. The disturbing factors then left to be dealt with

[1] Franklin Institute Journal, March 1919, p. 311.

would be the secondary scattering and earthlight. The influence of secondary scattering may be reduced very considerably by making the observations at the extreme red end of the visible spectrum. On a clear bright day, the sky as seen at a mountain observatory through a deep red glass appears almost perfectly black, but there is ample illumination, if the observer's eyes are carefully screened from extraneous light, to allow the extent of polarisation to be determined with the help of a double-image prism and a nicol. The effect of earthshine on the polarisation may be estimated by utilizing the data obtained by Luckiesh[1] on the albedo of different types of landscape from aeroplane observations. Under such conditions it should evidently be possible to eliminate the disturbing influences and to detect the residual effect due to molecular anisotropy.

24. In order to make a test on these points, the writer made the ascent of Mount Dodabetta (8750 feet above sea level) in the Nilgiris on the forenoon of the 4th December, 1921. The sky was beautifully clear, free from cirrus clouds and almost completely black as seen through a red filter. The weaker component of polarisation was found to have 13% of the intensity of the stronger component. According

[1] Frank. Inst. Journal, *loc. cit.*

to Luckiesh, the albedo of landscape covered by grass or fields varies from 0·05 to 0·10, and of landscape covered by woods from 0·03 to 0·05. That of barren land is greater, ranging from 0·10 to 0·20. It was estimated that the average albedo of the Nilgiris and the surrounding country could be taken as 0·08. As an outside estimate therefore, earthshine when the sun is 45° above the horizon would not give rise to an imperfect polarisation exceeding 4%. L. V. King has calculated the imperfect polarisation due to secondary scattering at the level of Mount Wilson (5886 feet) and found it to be 5% at the red end of the spectrum. The level of Mount Dodabetta is much higher (8750 feet) and the disturbing factors are therefore less, but some allowance must be made for the fact that the region of spectral transmission of the filter used extends to slightly shorter wave-lengths, and we therefore retain King's figure of 5% as the effect due to secondary scattering. A total of 9% out of the 13% actually observed is thus accounted for, and the remaining 4% is ascribable to molecular anisotropy. This is in good agreement with the latest experimental results of Lord Rayleigh obtained in the laboratory.

Polarisation of Twilight.

25. Another very interesting way in which the problem may also be dealt with is by observations on the polarisation of the sky immediately after sunset. In this case, it is not necessary to use any light-filters or to work at a mountain observatory, and the measurements may be made on any clear evening at a low-level station. If the polarisation of the light of the zenith sky in the evening is determined from time to time, it will be found that as the sun approaches the horizon and sinks below it, there is a rapid improvement in the completeness of polarisation, followed subsequently by a slow and steady deterioration with deepening twilight. Kimball [1] who observed the phenomenon suggests that the improvement of the polarisation is due to the earth-illumination being cut off when the sun sets. This explanation does not appear to be adequate as it does not account for the large magnitude of the effect or the rapidity with which it occurs. For instance, in some observations made at Calcutta by the author and by Mr. K. R. Ramanathan, it was found that 40 minutes before sunset the ratio of the intensities of the components of polarisation was 30 per cent., 20 minutes before sunset it was 20 per cent., at sunset it was 14 per cent., 20 minutes later it was 15 per cent., and then gradually rose again to 30 per cent. In view of the

[1] Mount Weather Observatory Bulletin, 1911.

low albedo of landscape already quoted above, we can hardly suppose that such effects could be merely due to the cutting off of earthshine. The greater part of the effect really arises in another way. As the sun approaches the horizon, the thickness of the atmosphere which his rays have to traverse rapidly increases, and the actual intensity of illumination of the first kilometer or two of the atmosphere above the observer becomes exceedingly small. At higher levels, however, the weakening of the sun's rays is not so great, and as we proceed upwards to the layers of the atmosphere in which the barometric pressure is considerably smaller than the sea-level value, the intensity of the sun's rays rapidly increases, until finally at a great height it reaches practically its noon-day value. The effective scattering layers of the atmosphere are thus its high-level dust-free portions. Thus immediately after sunset, the effect of the low-lying dust and of the earth-shine is automatically eliminated. Further, the great diminution in the effective mass of air and the increase in the effective wave-length of the transmitted rays which illuminate it should result in a considerable diminution of the effect of secondary scattering. It should also be noticed that the illuminating rays being horizontal, and the extension of the earth's atmosphere being chiefly horizontal, secondary scattering should have a much smaller influence than when the sun

is at a high altitude. This is easily seen on considering the directions of vibration in the incident light, in the primarily scattered light which reaches the observer, and in the scattered light arriving from different directions which after a second scattering also reaches the observer. In fact, a careful consideration shows that if the molecules of the atmosphere were spherically symmetrical, the zenith sky *immediately* after sunset should be almost completely polarised, the defect of polarisation if any, not exceeding 5 or 6 per cent. Actually, however, a defect of about 10% is observed even on the clearest days, showing that there is a residual effect of 4% or 5% arising from molecular anisotropy.

26. When the sun sinks very far below the horizon, much the greater part of the atmosphere above the observer enters the region of shadow and the influence of secondary scattering on the polarisation again becomes prominent. Some very curious effects may be observed, one of which is that the region of strongest polarisation in the sky, instead of following the movement of the sun, actually recedes from it.

The Problem of Secondary Scattering.

27. In attempting to extend the work described in the preceding pages to different wave-lengths in the spectrum and to put it on a very precise quantitative basis, we naturally come up against

the problem of evaluating the effect of secondary scattering on the polarisation. This had been attempted by Soret in order to explain the existence of "neutral points" in the sky.[1] More recent work is that of L. V. King already quoted in which he has used the theory of integral equations in order to find the result of self-illumination of the atmosphere. In order to apply his method to the determination of the state of polarisation of sky-light, King had to make two simplifying assumptions: firstly, that the effect of the curvature of the earth may be neglected: secondly, that the portion of the scattered radiation due to self-illumination is independent of the angle of polarisation of the incident radiation. As regards the first assumption, it should be remarked that it is the curvature of the earth that determines the horizontal extension of the portion of the earth's atmosphere which contributes the primarily scattered light which is again re-scattered by the part of the sky under observation. Its neglect is thus *prima facie* justifiable only if it can be shown that the actual brightness of the sky in a horizontal direction is the same as for an infinitely extended atmosphere. As regards the second assumption, we have only to remember the case just discussed—that in which the sun's rays are

[1] See Humphreys "Physics of the Air," Chapter on Optics of the Air.

nearly horizontal—to see that it may lead to results which do not agree with facts. It would seem therefore that there is a real need for a discussion of secondary scattering in which the curvature of the earth is taken into account and the result is fully worked out without any assumptions except perhaps the negligibility of multiple-scattering of the third and higher orders. If such calculations were made, it may prove possible to establish the imperfect polarisation for different wave-lengths due to molecular anisotropy by comparison with observations made at high-level stations. Perhaps the use of a simpler mathematical method than that adopted by Prof. King may render the problem tractable.

The Influence of Atmospheric Dust.

28. The curves showing the brightness of the zenith sky as a function of the wave-length obtained by the observations made at Washington and figured in Prof. King's paper show a sudden kink amounting practically to a discontinuity at a wave-length of 0·61 μ. A similar jump also occurs in the curves for polarisation of the zenith sky. In the curves for the Mount Wilson observations, undulations also occur but at a shorter wave-length, about 0·45 μ. These effects are clearly due to the influence of "dust," but precisely how they

arise does not appear to have been fully explained. The suggestion may be ventured that the effect is due to diffraction, the wave-length at which the bend occurs being determined by the average size of the dust-particles. In this connection, some interesting observations made by the author and by Mr. Bidhubhusan Ray may be quoted.[1] When suspensions of sulphur are used containing particles comparable in size with the wave-length, both the transmitted light and the scattered light show oscillations of intensity depending on the relation of size between the particles and the wave-lengths used, and the polarisation of the scattered light also shows striking fluctuations. It seems possible that dust may give rise to somewhat similar results in relation to atmospheric extinction, scattering and polarisation. At a higher level such as Mount Wilson, the average size of the particles remaining floating in the atmosphere would naturally be smaller and this would explain the occurrence of the bends at smaller wave-lengths in this case.

29. The foregoing suggestion is put forward for what it is worth. Careful experimental determinations of the average size of atmospheric "dust" at different levels would be necessary in order to establish its correctness.

[1] Proc. Roy. Soc., Oct., 1921, p. 102, and Proc. Ind. Assoc. for the Cultivation of Science, Vol. VII, Parts I and II, 1922.

Twilight and Afterglow.

30. A very interesting application of the theory of molecular diffraction is in the explanation of the various phenomena attending twilight or dawn, especially the manner in which the total illumination due to twilight diminishes with the movement of the sun below the horizon, the distribution of brightness in the different parts of the sky and its variation with the altitude of the sun, and so on. The impression appears to prevail that twilight phenomena are so complex in their nature that no simple calculations concerning them are possible. Thus for instance, Prof. W. J. Humphreys in his book on the Physics of the Air remarks, after giving an account of the various effects observed—"The foregoing descriptions which of course apply equally to dawn are by no means universally applicable. Indeed, the sky very commonly is greenish instead of purple, probably when the atmosphere is but moderately dust-laden. Furthermore, the explanations are only qualitative. A rigid analysis, even if the distribution of the atmosphere and its dust and moisture content were known,—which they are not, nor are they constant—would be at least difficult and tedious." With reference to these remarks, it may be pointed out, that twilight really arises from the illumination of the higher levels of the

atmosphere which may be regarded as dust-free, at least under normal conditions. Further, as we have seen in considering the explanation of the polarisation of twilight, the transmission of sunlight through the lower dusty levels is really negligible under these conditions, and practically the whole of the observed effect arises from light which has *throughout its course* passed through the higher levels. Hence, we are entitled to regard the problem as one of practically simple molecular diffraction, and the complications arising from secondary scattering are far less important than might be imagined. The possibility of giving a quantitative theory of twilight is therefore much less remote than has been suggested by various writers on the subject.

31. Kimball and Thiessen[1] have given data based on photometric measurements of clear sky, twilight and other natural illumination intensities on a fully exposed horizontal surface. These values are given in Table I.

TABLE I.

Relative Illumination Intensities. Surface of Illumination Horizontal.	Intensity in Foot candles.
Zenithal sun	9600·0
Twilight at sunset or sunrise ...	33·0
„ centre of sun 1° below horizon	30·0

[1] Monthly Weather Review, 44, p. 614, 1916.

TABLE I—*continued.*

Relative Illumination Intensities. Surface of Illumination Horizontal.					Intensity in Foot candles.
Twilight centre of sun		2°	below horizon		15·0
,,	,,	3°	,,	...	7·4
,,	,,	4°	,,	...	3·1
,,	,,	5°	,,	...	1·1
,,	,,	6°	,,	...	0·40
(End of civil twilight)					
		7°		...	0·10
		8°		...	0·04
		8°-40′		...	0·20
		9°		...	·015
		10°		...	·008

The above table shows that the brightness of twilight changes rapidly when the sun is more than about 4° below the horizon. The author has attempted to explain the observations of Kimball and Thiessen quoted in Table I quantitatively on the basis of molecular scattering. The method adopted is to divide up the whole atmosphere above the observer into a series of horizontal layers, and to find the effective mass of air in each layer illuminated by the direct rays of the sun, secondary scattering being neglected. In making the calculation, allowance must be made for the diminution of intensity of the sun's rays before they reach the air-mass under consideration, and the

cosine of the angle at which the diffracted rays illumine the horizontal surface of the photometer must also be included as a factor. Approximate methods of numerical quadrature were used, and it was found that the observations of Kimball and Thiessen were quite satisfactorily explained, at least as regards the relative values of the illumination for different altitudes of the sun after sunset. But as regards the ratio of full sunlight to the intensity of twilight a discrepancy appears which has not up to the time of writing of this volume been cleared up. It is possible that the discrepancy is in some way due to refraction of the sun's rays in passing horizontally through the earth's atmosphere. But this can only be settled by further investigation. Sufficient work has been done, however, to show that the problem of twilight at least in its essential features, is capable of being subjected to numerical computation of intensities from theory for detailed comparison with the observations.

CHAPTER IV

Molecular scattering in Liquids

32. As early as the year 1899, in his first paper on the scattering of light in the atmosphere,[1] the late Lord Rayleigh clearly emphasised the principle that his theory of molecular scattering is not applicable in the case of highly condensed media such as dense vapours, liquids and solids, for the simple reason that the molecules in them possess only a greatly restricted freedom of movement. The distribution of the molecules cannot in the circumstances be regarded as a simple random arrangement, and hence the phases of the scattered waves arising from the individual waves are not uncorrelated. The total energy scattered by a volume of a liquid or a solid cannot therefore by any means be equated to the sum of the energies scattered by the individual molecules in it. In the face of this clearest possible declaration of principles, some recent writers, notably Fowle,[2] and Cabannes[3] have put forward the obviously incorrect

[1] Phil. Mag., Vol. XLVII, pp. 375-384 (1899). Scientific Papers, Vol. 4, p. 397.

[2] Astrophysical Journal, Vol. 38, p. 392.

[3] Annales De Physique, Tome XV, pp. 1-150.

suggestion that Rayleigh's theory is applicable also in the case of liquids. How far such an assumption must be from the truth can be realised easily in the light of the discussion of fundamental principles contained in our first chapter. As we have seen, it is the degree of approximation of the compressibility of the medium to that given by Boyle's law which is the measure of the degree of applicability of the principle of random phase on Rayleigh's theory. As is well-known, the compressibility of a liquid or a solid is usually only an extremely minute fraction of what it would be if Boyle's law were applicable. This itself is sufficient to show that we shall be greatly in error if we attempted to extend the principle of additivity of the energy effects of the individual molecules to the case of liquids. In fact, Strutt has already found that liquid ether scatters a great deal less light than the vapour in proportion to the relative density of the two media.[1] We can easily see why this should be so. Owing to the near approach of the molecules to each other in the liquid state they occupy a large proportion of the total volume of the containing vessel. Hence the non-uniformity in their spatial distribution is far less striking than in the case of gases, and in consequence there is a partial correlation of the phases of the waves starting out from the individual

[1] About $\frac{1}{7}$th according to Strutt ; Proc. Roy. Soc., Vol. 95, p. 175.

molecules which entails as the result of interference, a great falling off in the total energy scattered. A very interesting calculation[1] which was made by Rayleigh of the energy scattered by a cloud of particles having a restricted freedom of arrangement clearly illustrates this principle.

The Einstein-Smoluchowski Theory.

33. The complexities of the problem of molecular diffraction in liquids are so great that we have evidently to proceed by statistical methods. Fortunately, this has already been accomplished in great measure in the beautiful "theory of fluctuations" developed by Einstein[2] and Smoluchowski[3] and used by the latter especially to explain the peculiar opalescence exhibited by fluids near the critical state. In this theory, scattering is considered not as due to individual particles but to small local variations of density arising from the heat movements of the molecules. These variations are quantitatively determined by Boltzmann's principle. Smoluchowski's statistical thermodynamical reasoning gives for the mean square of fluctuation of density in volume V of density ρ_0 an expression, which

[1] Phil. Mag., Dec. 1918, p. 449.

[2] Ann. der. Phys. 33 (1910), p. 1275.

[3] Ann. der Phys. 25 (1908), p. 205. Also, Epstein, Ency. Math. Wiss, Band V. 3, p. 520.

except in the immediate neighbourhood of the critical point is equal to[1]

$$(\overline{\Delta\rho})^2 = \frac{RT\beta_o\rho_o^2}{N_1 V} \quad \ldots \quad (1)$$

where R is the gas constant, N_1 is the number of molecules in a grammolecule, β_o the compressibility corresponding to density ρ_o equal to

$$-\frac{1}{v}\cdot\frac{dv}{dp}.$$

At right angles to the incident light the intensity of scattered light is given by the expression[2]

$$\frac{\pi^2 V^2 (\Delta\epsilon)^2}{2\lambda^4}\cdot\frac{1}{r^2}. \quad \ldots \quad (2)$$

$(\Delta\epsilon)$ being the variation of the dielectric constant.

Now as these individual local variations are irregularly distributed, the phases of the various scattered beams are also quite arbitrary, and hence for calculating the total intensity of scattered light we have merely to sum up the above expression over the total volume ϕ. The expression contains a factor

$$\Sigma(\Delta\epsilon)^2 V^2$$

which may be evaluated by use of the Mosotti-Lorentz law

$$\frac{\epsilon-1}{\epsilon+2} = \text{const. } \rho$$

[1] Boltzmann, Wien. Ber. 63, p. 397. A. Einstein, Ann. d. Phy. 19, p. 373.

[2] Rayleigh—Phil. Mag. 1881, p. 81.

Differentiating we obtain

$$(\Delta\epsilon)^2 = \frac{(\epsilon-1)^2(\epsilon+2)^2}{9} \cdot \left(\frac{\Delta\rho}{\rho_o}\right)^2. \quad \ldots \quad (3)$$

Substituting in this the value given above for fluctuation of density we obtain

$$\frac{(\epsilon-1)^2(\epsilon+2)^2}{9} \cdot \frac{RT\beta_o}{N_1} \cdot \geqq V$$

$$= \frac{RT\beta_o}{N_1} \cdot \frac{(\epsilon-1)^2(\epsilon+2)^2}{9} \cdot \phi \quad \ldots \quad (4)$$

Thus the intensity of light scattered by a cubic centimetre of fluid at right angles to the incident rays is

$$\frac{\pi^2}{18} \cdot \frac{RT\beta_o}{N_1} \cdot \frac{(\epsilon-1)^2(\epsilon+2)^2}{\lambda^4}$$

$$= \frac{\pi^2}{18} \cdot \frac{RT\beta_o}{N_1} \cdot \frac{(\mu^2-1)^2(\mu^2+2)^2}{\lambda^4} \quad \ldots \quad (5)$$

In the case of gases

$$\beta_o = \frac{1}{p} \quad \text{and} \quad \mu^2+2=3, \text{ nearly}$$

and μ differs only slightly from unity. The formula then reduces to Rayleigh's result. Equation (5) may be applied with confidence to find the intensity of light scattered in liquids, for the work of Perrin and others on the Brownian movement in liquids has furnished a strong confirmation of Einstein's fundamental work on the subject and has shown that the energy of translation of molecules in a liquid is the same as in the gaseous state of matter. The formula

thus expresses in a perfectly general manner the scattering power of a fluid associated with its ordinary refractivity taken together with the non-uniformity of optical density resulting from molecular movements. It is a point worthy of notice that according to the formula the scattering power of liquids is proportional to the absolute temperature, if we leave out of account the changes which would result from variation in compressibility and refractive index with temperature. The constant N_1 is a pure number independent of the particular state of molecular aggregation of the substance or its density.

34. It must be remembered of course, that the whole theory depends for its validity on Maxwell's electro-magnetic equations for the propagation of light, and the assumption of a continuous interaction between the molecules and the impinging light-waves.

Experimental Study.

35. To determine whether the absolute scattering power of liquids for light is correctly given by equation (5), some preliminary observations have been made by the writer and by Mr. K. Seshagiri Rao working in his laboratory at Calcutta. As is quite obvious, it is of the highest importance to get very pure liquids,

Water as is well known is difficult to get free from motes. On examination the ordinary tap water showed a very strong scattering when a beam of light was sent through it. The track was practically white and showed innumerable motes floating about in the water. Repeated filtration through several thicknesses of Swedish filter paper made an improvement, the track being now of a bluish colour, and a still better result was obtained when an earthenware filter was used. Suspended matter was however still in evidence, and the track was also much brighter when viewed nearly in the direction of the source than when seen transversely or in the opposite direction. A somewhat casual attempt was then made to clear the water by adding alkali and alum and thus throwing out a gelatinous precipitate of aluminium hydroxide. This made a further improvement, but small particles of the precipitate remained floating about, apparently because the depth of the water was insufficient and the appearance of the track of the beam was not very prepossessing. The next attempt was made with ordinary distilled water which had been prepared without any special precautions and stored for some time in the chemical laboratory. This gave immediately a much smaller intensity of light-scattering than the tap water had done after several attempts at filtration. For purpose of observation,

the distilled water was put into a stoppered glass bottle with square sides and allowed to stand. Test observations from day to day of the scattered beam with a double image prism and a set of Wratten colour filters showed a progressive improvement. After about a fortnight's standing, the track of the light was hardly conspicuous unless a dark background was provided for it to be viewed against, and the defect of polarisation at the violet end of the spectrum was much less striking than it was when the observations were begun. Small motes were still to be seen, particularly when viewed in the direction of the source, but the track was of a blue colour and it was judged that the greater part of the observed luminosity was probably due to the water itself. A sample of water which had been distilled at the Calcutta Mint and stored for 3 months also showed the blue track very well. Allowing it to stand for some time improved matters appreciably.

36. For a quantitative estimate, the brightness of the beam in the water was compared directly with that of its track in saturated ether vapour. The latter was contained in a pear-shaped bulb with a long neck which was covered over with black paint and formed the "black cave" against which the light scattered by the vapour was observed. The bottle and the bulb were set side by side and a parallel beam of

light passed through both. An Abney rotating sector was placed in front of the water bottle and the opening of the sector varied till the tracks appeared to be of equal intensity in both vessels as judged visually. The opening of the sector gives the ratio of intensities, a correction being made for the loss of light by reflection in the passage of the direct and scattered pencils through the glass walls. The determinations made in this way were not anything more than approximate estimates. The scattering of light in saturated ether vapour has been measured by comparison with air by Rayleigh and shown to be accurately proportional to the square of its refractivity. Using this result, the observation showed the scattering power of the sample of water used was 175 times that of dust-free air at N.T.P. From theory we find taking for air

$\beta = 0{\cdot}987 \times 10^{-6}$ cm^2 dynes^{-1} T$=273°$, $\mu = 1{\cdot}000293$ and for water at 30°c, $\beta = 43{\cdot}5\ 10^{-12}$ cm^2 dynes^{-1}, T$=303$, $\mu = 1{\cdot}337$

that volume for volume, water should scatter 140 times as strongly as air at N.T.P. This, though not agreeing exactly with the observed value is only slightly smaller and the difference may be explained as due to the effect of residual suspended particles in the water used in the experimental work.

37. More accurate measurements were made a month later by Mr. K. Seshagiri Rao when the sample of water had still further improved. The method used was the comparison of intensities by a double image prism and a nicol. Sunlight was used as the source of light and a long-focus lens was used to give an intense and nearly parallel beam. The two bottles were placed on either side of the focus and the track viewed through two parallel slits. The double image prism was placed so that the four images seen were in a line with the planes of vibration horizontal and vertical. The weaker image from the water was adjusted so as to appear just in contact with the stronger image from the ether vapour. By the nicol, these two were reduced to equality. The ratio was then given by $I_1/I_2=\tan^2\theta$ where θ is the angle through which the nicol is rotated from the zero position. Measurements by this method gave the ratio of scattering of water at 25° to air at N.T.P. as 158. The ratio was still higher than that given by theory. Possibly it might be due to the motes not having been completely eliminated. But it seems more probable that the higher ratio may be due to the anisotropy of the molecules of water which is evidenced by imperfectness of polarisation. According to the theory of Einstein and Smoluchowski, the light scattered in a direction perpendicular to the incident rays

should be completely polarised. As already mentioned in a previous chapter, the work of Cabannes and Strutt shows that most gases depart from this ideal sphericity of molecules. Cabannes has amplified Rayleigh's theory by considering the anisotropy of the molecule and shown that the expression for the intensity of scattered light should be multiplied by

$$\frac{6(1+\rho)}{6-7\rho}$$

where ρ is the ratio of the weak component of polarisation to the strong one. It is evident from the formula that the larger the value of ρ, *i.e.*, the greater the departure from sphericity, the greater is the intensity of scattered light. It is clear that a similar correction must also be made in the case of liquids. The value of ρ for the specimens of water used is 12% and for air 4%. When this correction is applied the theoretical ratio comes out at 160 and is in fair agreement with that actually observed.

Determination of the Avogadro Constant.

38. More accurate comparisons of intensities by photographic methods are in progress. It is also intended to measure the co-efficient of scattering absolutely using liquids completely freed from motes by repeated slow distillation in a vacuum. From a knowledge of the

absolute scattering power, the values of R, T, β and μ being known, it should be possible to calculate the Avogadro constant N_1 from experiments on liquids in much the same way as Cabannes has done with gases. The method by which it is proposed to measure the co-efficient of scattering is as follows. The intensity of the scattered light will be of the order of 10^{-7} of that of the incident beam. To make comparisons we have to reduce the intensity of the incident beam considerably and it is proposed to effect it in the following manner. A very short focus lens will be used to condense the light. The light coming to its focus will diverge very rapidly. The radius of the solar image at the focus will be of the order of a millimetre while at a distance of about 2 metres, owing to great divergence the intensity will have been reduced in the ratio of about 10^{-4} or 10^{-5}. Further reduction will be made by a rotating disc with a small radial slit at the edge. The width of the slit will be varied till the light incident on a fixed aperture placed behind it is reduced to the same intensity as the image of the track in the water, as determined by photography. Incidentally the λ^{-4} law will also be tested.

39. According to formula (5), the scattering power is proportional to the absolute temperature of the liquid apart from any variations in μ and β

due to the same cause. This effect should be particularly noticeable in the case of liquids such as ether whose compressibility increases rapidly with temperature. In the case of water, we should not expect much change as both the compressibility and the refractive index diminish with rise of temperature. These points are also under investigation.

Molecular Scattering and Transparency of Liquids.

40. Since the energy of the light laterally scattered is derived from the primary beam, there must result a certain attenuation in the intensity of the latter in its passage through the liquid, the magnitude of which may be readily calculated from the co-efficient of scattering. The multiplying factor necessary is $\frac{16\pi}{3}$ which represents the result of integration over a sphere completely enclosing an element of volume of the scattering fluid. The transmitted light is given by the formula $I = I_0\ e^{-\alpha l}$ where l is the length of the path traversed through the liquid and

$$\alpha = \frac{8\pi^3}{27} \cdot RT\beta_0 \frac{(\mu^2-1)^2(\mu^2+2)^2}{N_1\ \lambda^4}$$

As in the case of atmospheric scattering we may expect that the co-efficient of attenuation α will exactly indicate the observable

transparency of the medium in those parts of the spectrum for which it does not exercise any selective absorption. From the data already given and the known values of R, T, and N_1, α may be readily determined for any value of the wave-length.

41. From the observations of various experimenters[1] it is known that water exercises a selective absorption on the longer wave-length side in the visible spectrum and also in the ultra-violet region. Measurements of the co-efficient of absorption in water have been made by various investigators, but the values obtained by each are hopelessly different from those of others. Calculations on the basis of Evans's and Aschkinass' values show that water is actually six to ten times less transparent than it should be. It is not evident from their papers whether they had taken care to get the water mote-free. The most reliable measurements of any hitherto made appear to be those of Count Aufsess. This experimenter used double-distilled water and convinced himself that it was free from suspended matter. It was found by him that the selective absorption in the visual region ceased for wave-lengths less than 558 $\mu\mu$. For the two

[1] Evans : Proc. Roy. Soc. (1894), Vol. 57.
Aschkinass : Wied. Ann. 55 (1895).
Krenssler : Ann. der Phys. (1901), Band 6.
Aufsess : Ann. der Phys., Vol. 13, 1904; also Kayser's Handbuch, Vol. 3, p. 392.

wave lengths 522 $\mu\mu$ and 494 $\mu\mu$ Aufsess gives as the co-efficient of absorption 0·00002. For these two wave-lengths the co-efficient of attenuation β calculated from the formula given above is respectively 0·000022 and 0·000029. The agreement of observation and theory is significant. It is desirable that further accurate measurements for different wave lengths for carefully purified water up to the extreme violet end of the spectrum were available so that the increase of the co-efficient of attenuation inversely as the fourth power of the wave length could be tested. It would be interesting to determine by careful experiment whether the intensity of the light scattered by water follows the fourth power law exactly. It would be also interesting to investigate scattering at or near an absorption band and to investigate what becomes of the energy absorbed, whether it appears as selective scattering or is merely stored up in the liquid. If there is any selective scattering we might expect deviations from the fourth power law in that region of the spectrum.

Observations of Polarisation.

42. Reference has already been made to the imperfect polarisation of the light transversely scattered by liquids. The detailed results on this point will now be described. The

determinations of polarisation for water have been made by visual methods. Sunlight was used as the source of light and the track was viewed through a small rectangular aperture. The double image prism was so set that the two images were in line and just touching each other, and the directions of vibrations were horizontal and vertical. The two images were brought to equality by a nicol on either side of the zero position. Half this angle gave the angle θ through which the nicol was rotated from the zero position and the ratio of the two intensities was of course given by $\tan^2 \theta$. Measurements were made in different regions of the spectrum by using Wratten colour screens.

The results are given below—

Red.	Yellow.	Green.	Blue.	Violet.
13·2	10·3	11·5	15·3	21·7

Inspection of the values shows an increase of polarisation in the red and violet regions with a minimum value at the yellow. It is well known that water has an absorption band in the red and another in the ultra-violet. The experiments thus indicate that near the absorption bands the imperfectness of polarisation increases. It will be noticed that the figures show a rapid increase near the violet end of the spectrum. This may be partly due to the small particles still remaining suspended in the liquid

whose influence will only be greatly evident in the region of shorter wave-lengths. But that the phenomenon is real, is shown by the fact that at the red end where the influence of the particles is small there is a slight perceptible increase of polarisation. It would be interesting to make observations at and near the absorption bands, using carefully purified liquids. Another point worthy of investigation would be to observe what influence the temperature has on the polarisation. It is well known that water in liquid form exists as molecular aggregates and that temperature has a great effect on them. We might expect therefore a change of polarisation with temperature.

The Orientation of the Molecules.

43. It is important here to notice that imperfect polarisation of the transversely scattered light is noticed not only when the primary beam is unpolarised, but also when the latter is itself completely polarised. To test this point a nicol was placed so that the incident light passed through it. It was found that when the plane of polarisation was vertical or horizontal the scattered light was a maximum or a minimum respectively. In the latter case, that is, when the scattered light was a minimum, it was viewed through a second nicol and its intensity was

found to be independent of the plane of polarisation of the latter. It could however be extinguished by two nicols or a double image prism and a nicol, thus showing that it was unpolarised light. A similar phenomenon is also observed in the case of molecular scattering in gases and is a consequence of the fact that the *orientation* of the molecules in fluid media is arbitrary. The observed intensity of scattering is the resultant effect of molecules in all possible positions and orientations, so that the weaker component of polarisation stands in no definite relation of phase to the stronger component, in other words, the scattered light consists partly of *common* light. The intensity of the Tyndall cone as observed by a nicol when the primary beam is uupolarised is given by the relation $J = C_1 + C_2 \cos^2 \delta$ where δ defines the orientation of the plane of polarisation of the observing nicol.

Relative Scattering Power of Different Liquids.

44. The observations of Strutt with liquid ether, and of the present writer with Mr. Seshagiri Rao on water have clearly shown that the absolute scattering power of liquids is much smaller than that of the corresponding vapours making allowance for the difference of density.

This diminution is clearly explained on the Einstein-Smoluchowski formula as the result of the extreme smallness of the compressibility of the liquid which more than sets off the result of the increased refractivity. Naturally, therefore, we should also expect the Einstein-Smoluchowski formula to give the relative scattering power of different liquids correctly. The opportunity for testing this point is furnished by some recent observations of W. H. Martin on light-scattering by dust-free liquids.[1] Martin found a strong defect in the polarisation of the light scattered by all the liquids observed by him, the defect increasing with the light-scattering power. The Cabannes factor $\frac{6(1+\rho)}{6-7\rho}$ in the intensity is thus very important. The necessary data for compressibility and refractive index are not forthcoming for all the liquids experimented upon by Martin. So far as the available data permit, the results for the liquids listed in column I of the table below have been compiled and the relative scattering powers shown in column II without applying the Cabannes correction, and in column III after applying the Cabannes correction. It will be seen that the computed ratios in column III and those given by Martin's observations shown in column IV agree tolerably. It is to be noted

[1] Journal of Physical Chemistry, Vol. 24, 1920, p. 478.

TABLE II

WATER IS TAKEN AS THE STANDARD

I Liquid.	II Calculated from Einstein-Smoluchowski formula without correction.	III Calculated from formula with Cabannes's correction.	IV Experimental results of Martin.
Water ...	1·00	1·00	1·00
Ether ...	4·53	4·78	3·94
Methyl Alcohol	2·03	2·04	2·67
Ethyl Alcohol	2·86	2·87	3·00
Benzene ...	6·38	19·5	15·17
Toluene ...	5·60	17·1	16·6

that the Cabannes correction cannot be applied when ρ is more than 50%, and this maximum value must be used in the formula when the observed defect of polarisation exceeds 50%.

Transition from the Liquid to the Gaseous State.

45. As we have seen, the Einstein-Smoluchowski formula, when corrected for the effect of molecular anisotropy gives results in fair agreement with observations in non-fluorescent liquids, and it also automatically reduces to the Rayleigh formula in the case of gaseous media. Further, the formula which was originally developed in order to explain the observed

enormous light-scattering power of gases at temperatures slightly above the critical point has been quantitatively confirmed for this region by the very fine measurements of Keesom[1] on the opalescence of ethylene. In view of these striking successes of the formula, we may, *primâ facie*, feel confident that it would correctly represent the sequence of phenomena throughout the entire range of transition between the liquid and the gaseous states. But, surprisingly enough, the law seems to break down in the case of gases under high pressure. Strutt has shown experimentally that the scattering by saturated carbon dioxide at 21°C at a pressure estimated at 60 atmospheres and a density 114·7 times the density at atmospheric pressure is 102 times the scattering at the latter pressure. This agrees fairly satisfactorily with the Rayleigh formula. But when we calculate the scattering according to the Einstein-Smoluchowski formula, the value of the ratio is given by

$$\frac{\beta_1(\mu_1^2-1)^2(\mu_1^2+2)^2}{\beta(\mu^2-1)^2(\mu^2+2)^2}$$

where β_1 and μ_1 refer to carbon dioxide under pressure and β and μ refer to the gas at ordinary pressure.

46. In the following calculation, the unit of pressure is taken to be 1 atmosphere.

Now $\beta=1$

and $\mu-1$ at 21°C[1] $=4{\cdot}50\times10^{-4}\times\frac{273}{294}$

[1] Annalen der Physik, 1911, Band 35, p. 591.

We may put $(\mu^2-1)=2(\mu-1)$
and $\mu^2+2=3$

$$\therefore \beta\,(\mu^2-1)^2(\mu^2+2)^2=6{\cdot}29\times10^{-6}.$$

The compressibility of the condensed vapour may be obtained in either of two ways; one, by making use of the experimental isothermal of CO_2 for 21°C and the other by calculation on the assumption of a suitable equation of state. The value of β obtained from Andrews' isothermal curve [2] 23·5° is $\frac{1}{77}$. On assuming Clausius' equation of state

$$\left(p+\frac{a^1}{T(v+c)^2}\right)(v-b)=RT$$

(which is found to represent the isothermals of CO_2 at high pressures with great accuracy [3]), we get for the co-efficient of compressibility

$$\beta=-\frac{1}{v}\frac{dv}{dp}=\frac{v-b}{v}\quad p+\frac{a^1}{T(v+c)^2}-\frac{2a^1(v-b)}{T(v+c)^3}$$

Taking $p=60$ atmos.

$v=\frac{1}{115}$ of the volume at the atmospheric pressure at 21°C

$=\frac{1}{115}\cdot\frac{294}{273}$ of the volume at 0° C.

and the constants

$a=2{\cdot}092$
$b=0{\cdot}000866$
and $c=0{\cdot}000949$

We get $\beta_1=\frac{1}{18{\cdot}1}$

[1] Kaye and Laby's Tables.
[2] Phil. Trans. Roy. Soc., p. 575, Part II, 1869.
[3] Jeans : Dynamical Theory of Gases.

We may take the mean of these results $\frac{1}{17{\cdot}5}$ as the compressibility of the vapour at 21°C.

The value of μ_1^2 is easily calculated from the data given by Dr. Phillips.[1]

It comes out to be 1·099 and the value of

$$\beta_1(\mu_1^2-1)^2(\mu_1^2+2)^2 \text{ to be } 5{\cdot}38\times10^{-3}$$

Hence

$$\frac{\beta_1(\mu_1^2-1)^2(\mu_1^2+2)^2}{\beta(\mu^2-1)^2(\mu^2+2)^2} = \frac{5{\cdot}38\times10^{-3}}{6{\cdot}29\times10^{-6}}$$
$$=855.$$

whereas the actual scattering observed by Strutt was only 102. It seems very remarkable that a law which holds good for such widely different conditions as (1) a gas at ordinary pressures, (2) in the immediate neighbourhood of the critical point and (3) for liquids, should not also hold good for saturated vapours below the critical temperature. The reason why the law apparently fails is not clear. The question is one of very great importance and its solution may be expected to throw light on the mechanism of scattering. What is urgently wanted is a careful determination of the scattering co-efficient over a wide range of pressures and temperatures, from the state of vapour through the critical point to the liquid. If it is indeed found that Strutt's results are confirmed for the whole region of temperatures and pressures below the critical point, it might mean that the arrangement of

[1] Phillips : Proc. Roy. Soc. A 97, p. 225.

the molecules in space is of far less importance in determining the phase of the scattered waves than is assumed in the treatments so far given, and that the attempt to explain the molecular scattering of light on the basis of the classical theories of electromagnetic wave-propagation and the continuous interaction between light and the electrons is really a failure. We may then be forced to adopt explanations based on a discontinuous type of action, exactly as in the theories of photo-electricity, ionization, and so on.

47. A related question is the imperfect polarisation of the scattered light. In all the cases investigated by the authors and by Martin, the scattered light from the vapour is found to be more perfectly polarised than that from the liquid. Why this should be so is not clear. There are no observations available regarding the polarisation of the light scattered by vapours under pressure. The changes in the polarisation of the scattered light in the transition from the gaseous to the liquid state should be investigated side by side with its intensity.

48. The discussion given here has perhaps raised more difficulties than it has solved. But this only demonstrates the importance of the subject and the need for an extended study of the phenomena both from an experimental and a theoretical standpoint.

CHAPTER V

The Colour of the Sea and the Albedo of the Earth

49. To an observer situated on the moon or on one of the planets, the most noticeable feature on the surface of our globe would no doubt be the large areas covered by oceanic water. The sunlit face of the earth would appear to shine by the light diffused back into space from the land and water-covered areas. The character and intensity of the radiation thus sent back would depend on various factors: firstly, sunlight diffused back by the gases of the atmosphere over the whole surface of the earth:; secondly, the sunlight incident on the oceans and returned partly after reflexion at the surface of the water, and partly after diffusion within its body; thirdly the light reflected back from cloud-covered areas and the lower dusty levels of the atmosphere; and fourthly, the light scattered by the land-masses. When we consider the fact that nearly three-quarters of the surface of the globe is covered by oceanic water, we begin to realise that the molecular scattering of light in liquids may possess an astronomical significance, in fact contribute in an important degree to the observed

albedo of the earth. The "earthshine" on the moon for instance may owe not a little to the light diffused out from the oceanic water as the result of molecular diffraction.

50. In intimate relation with the problem of the albedo of water stands the question of the colour of the sea. A detailed discussion of the subject is appearing in a separate paper,[1] and it is sufficent here to deal with the matter only so far as it illustrates the theoretical principles of our subject.

Colour and Polarisation of the Light Scattered in the Sea.

51. The method of observation used by the writer is sufficiently described in a preliminary communication that appeared in *Nature*,[2]:—As Tyndall and others have remarked, the reflection of sky light at the surface of the water is an embarrassing feature in making observations of the colour of the sea. Its influence may however be eliminated in the following simple way. Light reflected at the polarising angle from the surface of a liquid may be quenched by observation through a suitably oriented Nicol. Hence by observing a tolerably smooth patch of water through a Nicol at the polarising angle, the surface-reflection may be got rid of. The Nicol

[1] Proc. Roy. Soc. 1922.

[1] Nature, November 17, 1921. p. 367.

may be mounted at the eye-end of a card-board tube so that it can be conveniently held at the proper angle with the surface of the water and rotated about its axis so as to get the correct position for extinction of the reflected light. During a recent voyage, the writer made some observations by this method in the deeper waters of the Mediterranean and the Red Seas and found that the colour of the sea so far from being extinguished when the sky-reflection is cut off, is seen with wonderfully improved vividness and with saturated hues. Even when the water is ruffled or when it is viewed more obliquely than at the polarising angle, the Nicol helps to weaken the sky-reflection. Further, as is well-known, the light of the sky is itself strongly polarised, and this fact may, in favourable circumstances be used to practically eliminate sky-reflection from the whole surface of the sea. For this purpose, the time most suitable is when the sun has reached its maximum altitude and the observer should stand with his back towards the sun and view the surface of the sea through a Nicol. The part of the sky facing the observer has then its maximum polarisation, especially the low-lying parts, and the amount of polarisation is further enhanced when the light is reflected from the water at various angles of incidence. By turning the Nicol about its axis, the best position for extinction should be found

and the whole surface of the sea will then be found to glow with a vivid blue light emerging from inside the water. Part of this improvement is also due to the fact that the Nicol in great measure cuts off the atmospheric haze which covers the more distant parts of the sea.

52. The obvious way of testing the light from the sea for polarisation, that is, viewing it through a Nicol and turning the latter about its axis, is interfered with by the fact that the intensity of the reflected light also varies at the same time and obscures the variation in the intensity of the light diffused from inside the water. Even thus however, it is possible to observe the polarisation of the scattered light, the surface of the water appearing *less* blue when seen through the Nicol in one position than when viewed directly. Much the better way of detecting the polarisation of the diffused light, however, is to hold the Nicol at the proper angle for extinguishing the surface-reflection from the water and vary the *azimuth* of observation relatively to the direction of the sun's rays entering the liquid. Striking changes in the colour and intensity of the light diffused by the water will then be noticed. The best time for making this observation is when the altitude of the sun is moderately large but not too great. Obviously, if the sun's rays are too nearly vertical, varying the azimuth of observation can make

no difference. But when the sun's rays inside the water proceed at an angle to the surface, the variation of the azimuth of observation alters the relation between the direction of the primary beam and the scattered rays under test. When the observer has his back to the sun, he looks down practically along the track of the rays inside the water and the scattered light reaching his eye is unpolarised inside the water and is not extinguished in any position of the Nicol. The colour of the scattered light is then seen as a vivid but comparatively lighter blue. As the azimuth of the plane of observation is swung round, the intensity of the scattered light diminishes and its colour changes to a deeper blue, until finally when the observer nearly faces the sun,[1] the intensity of the scattered light is very small and it appears of a dark indigo colour. If the polarisation of the scattered light were complete and the direction of observation exactly transverse to that of the primary beams inside the water, the Nicol would have completely quenched the light. This is however not actually the case, evidently because we have to deal not only with the scattering of the sun's direct rays inside the water, but also with multiply-scattered

[1] He cannot of course exactly face the sun as the reflection of the sun's rays from the surface of the water would then interfere with the observations. It is advantageous to choose a time when the altitude of the sun is such that these reflections are also quenched by the observing Nicol.

light and also with the blue light of the sky which enters the water and is then re-scattered within it. It is evident that these contributions to the luminosity of the water would diminish the perfectness of the polarisation [1] and would give a much darker blue than the primarily scattered rays.

53. The relatively deep colour of the secondarily scattered rays mentioned in the preceding paragraph is also prettily illustrated by observing the water on the shadowed side of the ship where the sun's rays do not strike it directly. Such water shows a much darker and deeper colour than the contiguous parts exposed directly to the sun's rays. A similar explanation may be given of the deepening of the colour of the sea as the sun goes down. The lower the altitude of the sun, the more important is the contribution of sky-light re-scattered within the water to the observed luminous effect. The blue colour of the sea as observed with the aid of a Nicol when the sky is completely overcast by clouds also appears of a distinctly deeper tint than sunlit water. It is probable that this may, at least in part, be due to the importance of multiple scattering in such cases.

[1] Much in the same way as the polarisation of sky-light even at 90° from the sun is incomplete. The imperfectness of the polarisation of the molecularly-scattered light (due to asymmetry of the molecules or other cause) also contributes to this result.

54. The difference between the colour of the parts of a wave sloping towards and away from the observer is a very interesting feature. When the surface of the sea is viewed through a Nicol, the degree of contrast varies enormously as the Nicol is rotated about its axis. The precise effect, of course, depends upon the relative intensity, colour and polarisation of the light reflected from the surface of the water at different angles and of the light emerging from inside the water. Broadly speaking, the phenomenon observed is that in one position of the Nicol the sea appears almost flat and undisturbed and in another position ruffled and full of ripples. The visibility of the horizon which depends on the contrast between sea and sky also varies, in some cases very greatly, as the Nicol is rotated.

The Albedo of Deep Water.

55. The phenomena described above make it perfectly clear that the light molecularly diffused from within the water is the principal factor to be taken into account and that the colour of the deep sea is not due to reflected sky-light as has sometimes been suggested. That the reflection of skylight is at all noticeable arises from the fact that the observer on the deck of a ship views by far the greater part of the surface of the sea at a very oblique angle. The position

would be entirely different in the case of an observer at a great height above the surface of the water, *e. g.*, when flying in an aeroplane. Since the reflecting power of water at normal incidence is quite small (only 2%), the luminosity of the sea to such an observer would be almost entirely determined by the diffusion of light within the water.

56. That such diffusion must, in the case of the deeper oceanic waters at any rate, be due to *molecular scattering* and not to any suspended matter may be inferred from the known great transparency and freedom from turbidity of such waters. It is extremely unlikely that, under normal conditions at any rate, any colloidal matter would remain for long in suspension in salt water. Further, it should be remarked that if sea-water did contain any "motes" in suspension, they would not appreciably influence the observed results. For, "motes" scatter light in an unsymmetrical manner, that is far more in directions approximating to that of the primary rays, and very little in the opposite direction which, to an observer above the surface of the water, is the direction that really matters.

57. A simple calculation may be easily made of the albedo of oceanic water. Since in round numbers, water diffuses light 150 times as strongly as an equal volume of air, a layer of

the liquid 50 meters deep would scatter approximately as much light as $7\frac{1}{2}$ kilometers of homogeneous atmosphere, in other words, it should appear nearly as bright as the zenith sky. This calculation however omits to take into account two important factors, the diminution in the intensity of sunlight before it reaches the level of the water and its further attenuation in the passage through the liquid and also the loss in intensity of the scattered light before it re-emerges from the depths. It is the two last factors just mentioned which together with the magnitude of the scattering itself ultimately determine the total observed luminosity of an ocean of liquid of very great depth. Neglecting the effect of self-illumination within the liquid and also the contribution which is made by diffuse sky-light which enters the water and is then subsequently re-scattered within the liquid—both of which may, in certain circumstances, rise to importance—the observable luminosity of a very deep layer of liquid may be readily calculated. For simplicity, we shall consider a case in which the altitude of the sun is sufficiently great to enable its rays within the water to be treated as approximately vertical in direction, and the intensity of the light scattered will also be assumed to be observed in an approximately vertical direction, *e.g.*, by an observer in an

aeroplane flying at some height above the water. The coefficient of scattering in such a case will be twice as great as when the scattering is observed laterally. Denoting it by $2B/\lambda^4$ and the coefficient of absorption of light in water by γ, the total observed luminosity is given by the integral

$$\frac{2B}{\lambda^4}\int e^{-2\gamma x}dx$$

x being the depth of any layer. For a sufficiently great depth this reduces to $B/\gamma\lambda^4$. For the case of pure water, the values of γ are taken from the determinations of Count Aufsess for wave-lengths up to 522 $\mu\mu$, and for shorter wave-lengths we may take them to be the same as the value of coefficient of attenuation α given by theory. The value of B is in round numbers 140 times the coefficient of lateral scattering by dust-free air. From these data and making an allowance for the diminution of the solar intensity in transmission through the atmosphere as on an average day, the total luminosity of deep water for different wave-lengths is expressed in Table III in terms of the kilometers of dust-free air at atmospheric pressure which would by lateral scattering of full sunlight give an equal effect.

TABLE III

ALBEDO OF DEEP WATER

λ in $\mu\mu$	658	622	602	590	579	558	522	494	450	410
Equivalent kilometers of dust-free air.	0·4	0 5	0 6	1·3	2·4	2·8	45	36	22	14

58. If we take the scattering by 8 kilometers of dust-free air as the standard and compare with it the figures shown in Table III, it is seen that in the light returned by the water, practically all the red is cut out, the orange and yellow are quite feeble, but the green is greatly enhanced, and also the blue, indigo and violet but to a considerably less extent. The standard of comparison,—(scattering by dust-free air) being itself of a blue colour, it is clear that the cutting out of the red and the enfeeblement of the orange and yellow would result in the colour of the light scattered by the water being a highly saturated blue. The enfeeblement of the orange and yellow would however considerably diminish the visual intensity which at a rough estimate would probably not exceed two or three times that of the zenith sky.

59. It will be understood from the figures given in Table III, that the blue colour of the light scattered by the water arises primarily from the operation of the Rayleigh λ^{-4} law, the

absorption of the red and yellow regions of the spectrum in the water resulting merely in the colour being more *saturated* than it would otherwise be. If the figures entered in the columns of Table III had represented ratios of comparison with *white* light, the presence and predominance of the green would result in the perceived colour being a greenish-blue and not a deep blue colour. In other words, the blue colour of the scattered light is really due to diffraction, the selective absorption of the water only helping to make it a fuller hue.

60. In connection with the foregoing calculations, it should be remarked that certain disturbing factors may arise. If owing to the presence of organic or other dissolved matter in the sea with a marked absorption in the green-blue region of the spectrum, the transparency of the water in this region be greatly diminished, the albedo of the deep water may show a great falling off. This is a possibility that should not be overlooked, and how far it does actually arise can only be determined by actual observation. But the considerations set out above make it clear that the light molecularly scattered in the oceanic waters must play an important part in determining the total fraction of the sunlight incident on the earth's surface that is diffused back into space. A fuller discussion of the matter would obviously be of great interest.

CHAPTER VI

Scattering of Light in Crystals

Introduction.

61. The well-known influence of temperature ("Debye-effect") on the intensity of X-ray reflection as illustrated, for instance, in the experiments of Sir W. H. Bragg[1] on rock salt indicates that the atoms in the space lattice forming a crystal are not absolutely fixed but oscillate to some extent about a mean position; the magnitude of this effect differs widely for different crystals depending on the value of the "characteristic temperature" for the substance. Larmor[2] has suggested that this thermal movement of the atoms in the crystal should have an important consequence, namely that when a pencil of ordinary light traverses a transparent crystal, a certain portion of the incident energy should appear as scattered light. Such an effect, if observable, would furnish us with direct visual evidence of the reality of thermal oscillations in solids. No theoretical calculation of the magnitude of the expected effect has however

[1] Phil. Mag. Vol 27, 1914, page 891.
[2] " " " 37, 1919 page 163.

appeared so far. Prof. R. J. Strutt[1] (now Lord Rayleigh) who experimented on the subject of the scattering of light in solids found that the track of a beam of light passing through a block of transparent quartz could be detected by photography and estimated that clear quartz scatters light 8 times as strongly as dust-free air. The effect was however ascribed by him to inclusions which he assumed were present in the quartz and not to the crystal itself. It occurred to the present author that observations with crystals such as rock-salt which show a marked Debye-effect would be of interest and that such crystals may be expected to show a strong scattering of ordinary light capable of direct visual observation. This expectation is shown to be justified by experiment, and it is found that even in the case of quartz in which owing to its high characteristic temperature the effect is weaker, direct visual observation of the scattering is possible.

Theory.

62. A theoretical discussion shows that the observed effects are of the expected order of magnitude and are thus really due to the thermal agitation of the atoms in the crystal and not to the presence of inclusions in the crystal. The

[1] Proc. Roy. Soc. Vol. 95, 1919, page 479.

principles on which we must proceed become clear when we consider the hypothetical case of a crystal in which the atoms occupy fixed positions on a space-lattice, thermal movements being assumed to be non-existent. The size of a cell in the lattice being small compared with the wave-length of the incident light, the crystal may for practical purposes be regarded as a continuous homogeneous medium of *uniform optical density* and can accordingly scatter no light. As thermal movement disturbs the uniformity of the medium and introduces local fluctuations of optical density, the medium is no longer homogeneous but shows irregular variations of refractive index, which though small, nevertheless in the aggregate, result in an appreciable scattering of the light traversing the medium. The intensity of this scattering can be calculated if the average magnitude of fluctuation of optical density is known.

63. It has already been pointed out in the chapters on scattering in gases and liquids that precisely the same considerations result in the Einstein-Smoluschowski formula for the scattering power, namely,

$$\frac{\pi^2}{18}\frac{RT\beta}{N_1\lambda^4}(\mu^2-1)^2(\mu^2+2)^2$$

where β is the compressibility, μ the refractive index of the substance, λ is the wave-length of

incident light and R, T, N_1 are the constants of the kinetic theory.

64. The success of Debye's theory in explaining the influence of temperature on X-ray reflection by crystals suggests that the Einstein-Smolu-chowski theory (which is based equally with Debye's theory on the principles of statistical mechanics) should enable the scattering power of crystalline solids for ordinary light to be determined. An important reservation is however necessary owing to the known failure of the law of equipartition of energy in the case of substances with a high characteristic temperature such as diamond. The formula for the scattering power deduced on the assumption that the translatory kinetic energy of the individual atoms in the space-lattice is the same as that of the freely moving molecules in gases and liquids would obviously give us a result much in *excess* of the actual values.

65. The scattering power being directly proportional to the thermal energy, it is clear that in order to obtain the correct result, we should diminish the value given by the formula in the ratio which the actual heat-content of the solid at the temperature of observation bears to the heat-content determined on the principle of equipartition of energy. A calculation made on this basis and from the known compressibilities and refractive indices gives a scattering

power for quartz about 10 times and for rock-salt about 40 times that of air at N.T.P.

Visual observations of scattering in crystals.

66. In view of the fact that the scattering of light in dust-free air is easily visible, it is clear that the observation of the scattering of much greater magnitude in crystals indicated by the theory should be a simple matter provided the conditions necessary for success are attended to. Sunlight is evidently the best source of light to use in carrying out the experiment. A beam of it being admitted into a darkened room through an aperture and then focussed by a lens, the crystal is placed at the narrowest point of the cone of rays. In examining valuable material, it is a good plan to use a filter to cut out the heat rays to avoid possible damage to the crystal. It is not at all necessary to use a large block of crystal. In fact quite a modest-sized piece of good quality will do, but it is of the highest importance that all the faces of the crystal should be scrupulously clean and highly polished so that they do not scatter light. The most suitable shape for the block is a cube or a rectangular parallelopiped held with one pair of faces quite square to the incident beam of light, the track of the cone of light inside the crystal being observed through another pair of

faces. A natural cleavage block of transparent rock-salt thus seems very suitable for the observations. If a crystal, say of quartz, is of irregular shape or has oblique faces, a good plan of getting rid of stray light is to immerse the block in a square glass trough containing *clean* distilled water. A dark background should be provided against which the track of the light passing through the crystal should be viewed. Working in this way the scattering of light in clear colourless quartz is very readily observed visually. The Tyndall cone is quite uniform and of a beautiful blue colour closely matching that of the track of a concentrated beam of sunlight in saturated ether vapour, and of about a third of its intensity so far as can be judged visually. The latter furnishes a convenient standard of intensity, and the observed result is thus of the order expected on theoretical grounds. Accurate measurements by a photographic method are at present being made in the author's laboratory by Prof. Lalji Srivastava.

67. By a similar method, light-scattering in rock-salt and in block ice can be very readily observed, the track being of a blue colour. In Iceland spar, the track is of a reddish tinge due apparently to a feeble fluorescence. This may be quenched by a suitable filter.

Polarisation of the Scattered Light.

68. In making observations on the polarisation of the light scattered in crystals, account has to be taken of the doubly-refractive or optically active property of the material. In the case of quartz, the difficulty may be avoided by sending the beam of light in a direction transverse to the optic axis, and observing in a direction transverse to the axis as well as to the track of the primary beam. Using this method, it is found that the light scattered transversely in quartz is not completely polarised, the track being quite clearly visible through a nicol. The cases of other crystals have not yet been thoroughly examined.

69. There is a noteworthy feature in which the light-scattering in crystals arising from the thermal movements of the atoms stands on a somewhat different footing from the case of light-scattering in liquids or gases. It has already been remarked in dealing with fluid media that the transversely-scattered light consists in part of *common* or *unpolarised* light even when the primary beam itself is completely polarised to begin with, and that this effect arises from the arbitrariness of the orientation of the molecules in such media. In crystals on the other hand, according to the current ideas, the positions and orientations of the atoms are

more or less definitely fixed, subject only to small oscillations about the mean positions. If this be the case, we should expect that if the primary beam in the crystal is itself polarised, the transversely scattered light should also be polarised, though not necessarily in the same way as in the case of spherically symmetrical atoms. Observations have been made by the writer to test this point. In order more readily to detect the residual intensity of the track of the beam in the crystal, the method of " flicker " was used. The track was caused to vibrate slowly up and down in the crystal so that its existence or non-existence could be detected. It was found that the track of the beam could almost completely be quenched by observation through a nicol when the primary beam was itself polarised. But if the incident light was unpolarised, it always remained quite clearly visible in any position of the observing nicol. The matter however remains to be further tested by photographic methods.

Possible Influence of Temperature.

70. As in the case of the Debye-effect, we should expect the light-scattering power of the crystal to be enhanced by rise of temperature. Some preliminary observations made with rock-salt seem to indicate that there is such an effect.

The technique of experimentation on light-scattering with crystals placed in enclosures capable of being heated up or lowered in temperature without damage to the surface of the crystal requires however to be further developed.

CHAPTER VII

Scattering of Light in Amorphous Solids

71. The methods of examination by the use of X-rays introduced by Laue and by Professors Sir W. H. Bragg and W. L. Bragg have thrown much light on the problem of the structure of crystalline solids, but our information regarding the structure of amorphous solids like glass is still scanty. What information we do possess, we owe to the recent work of Debye and Scherrer by the X-ray powder method. They find that most solids hitherto classified as amorphous are really composed of a large number of minute crystals. Dehydrated colloidal silica and stannic acid show the presence of such crystalline aggregates in an otherwise amorphous medium. Optical glass alone, of all the solids investigated, does not show any crystalline inclusions. Its diffraction photograph is exactly the same as that of a liquid.

72. The essential difference, then, between a crystal and an amorphous solid is that, in a crystal, the atoms are similarly oriented and arranged in a perfectly regular manner, whereas, in an amorphous solid, there is no regularity of arrangement of the molecules and there may even be local fluctuations of density as in a

liquid; only, these local fluctuations do not alter rapidly with time as in the case of liquids, but remain quasi-permanent for very long periods of time. Why a mixture of complex silicates like glass develops the phenomenon of rigidity to such a high degree in a non-crystalline condition, awaits explanation.

73. If, then, glass is an undercooled liquid, we should expect the scattering power of glass for ordinary light to approximate to that of a liquid rather than to that of a crystal. Lord Rayleigh in his paper on "Scattering by Solid substances," mentions that a specimen of Chance's Optical Glass showed a scattering about 300 times that of dust-free air. He was, however, inclined to attribute the scattering to inclusions and explained the observed imperfectness of the polarisation of the scattered light as due to the large size of the included particles. In view of the fact that the closest scrutiny under a powerful microscope even with dark-ground illumination, fails to indicate the presence of any visible inclusions, and in view of Debye and Scherrer's X-ray analysis of optical glass, it seems more reasonable to assume that the scattering is really molecular. Its magnitude is much larger than in the case of clear crystals and agrees with what might be expected on the basis of a non-uniform distribution of molecules such as would have existed in the liquid state

at the temperature of solidifaction of the material. Lack of data regarding the compressibility of melted glass at high temperatures makes it impossible to make a quantitative calculation of the scattering co-efficient on the basis of the Einstein-Smoluchowski equation. Observations made in Calcutta on a specimen of optical glass show a scattering power nearly four times that of pure water at ordinary temperatures. The track of a beam of sunlight is sky-blue in colour and is nearly, but not completely, polarised when viewed in a transverse direction. It does not show any fluorescence. (Many specimens of common glass exhibit a green, yellow or pink fluorescence when a beam of sunlight is sent through them; such fluorescence can be easily detected by examining the scattered light through a double image prism, when the two images would show different colours.)

74. Quantitative studies of the intensity and polarisation of the light scattered by well-annealed glasses of known composition at different temperatures would yield results of value regarding the molecular structure of glasses and of amorphous bodies in general. Experiments on the scattering of light in fused quartz of optical quality would also be of special interest in view of the recent observation of Rayleigh that this material exhibits a feeble double-refraction.

CHAPTER VIII

The Doppler Effect in Molecular Scattering

75. In the discussion of fundamental principles contained in our first chapter, we have already had occasion to refer to the Doppler effect arising from the uncoordinated movements of the molecules and found that it has no influence on the proportion of energy laterally scattered. We may now briefly consider the question whether it has any effect on the refractivity of the medium. The light scattered by a stationary molecule has the same wave-length in all directions as the incident radiation; and if we leave out of account the question of polarisation, there is no direction specially favoured as regards intensity as well. But in the case of a moving molecule, the wave-length of the scattered light is smaller in the direction of motion than in the opposite direction or intermediate directions. Since the molecule receives the incident radiation with an altered frequency, its motion must, according to the Rayleigh law of scattering, alter the *intensity* of the scattering, the latter being increased when the molecule moves against the advancing waves and decreased when it

moves with the advancing waves. The velocity of the scattered waves is however independent of the movements of the molecules, and hence the phase-relation between the advancing primary and secondary waves remains unaffected. The coherence of the primary and the scattered waves in the direction of propagation of the former on which the refractivity of the medium depends continues therefore to subsist. Any alteration in the scattering power of a molecule must produce a corresponding alteration in its contribution to the refractivity of the medium. If we assume that the movements of the molecules occur in random directions, the increased scattering and refractivity due to the molecules moving up towards the incident light is completely set off by the decreased scattering and refractivity due to the molecules moving in the opposite direction, and hence the refractivity of the medium considered as a whole remains unaffected. If however all the molecules have a common direction of movement relative to the advancing primary waves, the case is entirely different. If the molecules move against the direction of propagation of the primary waves, the scattering by all of them is increased and hence also the refractivity of the medium. If the molecules move with the waves, the scattering is diminished and therefore also the refractivity. In other words, the velocity of light

through the medium is increased or decreased by a certain proportion of the common velocity of its ultimate particles. This is exactly Fresnel's principle of the convection of light in a moving medium, and in a paper appearing in the Philosophical Magazine, Dr. Nihal Karan Sethi and the present writer have shown that the convection of light (Fizeau effect) in moving gases can be explained in this way, and we obtain (at least in the case of gases where the molecules can be regarded as independent centres of secondary radiation) a convection co-efficient agreeing with the values given by Fresnel's well-known expression and by the Theory of Relativity. The extension of the same argument to the case of liquids and solids will probably not present insuperable difficulties.

Experimental Observations of Doppler Effect.

76. As is well-known, the Doppler effect in the light reflected from a system of moving mirrors was demonstrated experimentally by Belopolsky and later by Prince Galitzin, and Stark's work on the Kanalstrahlen has also established the effect in the light emitted by electrically luminescent moving molecules. Recently Fabry and Buisson[1] have greatly simplified the laboratory demonstration of the Doppler effect by using a

[1] Journal de Physique, Tome 9, 1920, pp. 234-239.

rapidly-revolving paper disk, the edge of which is illuminated by a mercury lamp and observed through an etalon. It appears to the author that it would be interesting and quite practicable to make an experimental study of the Doppler effect in light *scattered* by moving molecules. The experimental arrangements most suitable would probably be very similar to those adopted in Fabry and Buisson's experiments. A flat revolving steel vessel containing compressed carbon dioxide or some suitable liquid may be provided with glass windows through which monochromatic light is admitted into it, the scattered light being observed laterally. By photographing the scattered light through an etalon and reversing the direction of rotation, the alteration of wave-length should be capable of observation. Simpler still would be to experiment with the light internally scattered within a rapidly revolving disk of glass. It would also be interesting to find in such cases whether there is any difference in the behaviour of molecularly scattered light and of fluorescent radiation.

77. The widening of the lines in the spectrum of a luminous gas due to the Doppler effect arising from the thermal movements of the molecules in it has been discussed by several writers, notably by the late Lord Rayleigh, and has been established by laboratory experiments.

It would appear worth while to examine experimentally the similar effect which may be expected to arise in the light *scattered* by a gas at high temperature. Light from a source at low temperature may be passed through a compressed gas or a liquid at a high temperature and the width of the lines in the spectrum of the scattered light determined by photographing it through an etalon or echelon spectroscope. The magnitude of the effect that may be expected has been discussed theoretically at the suggestion of the author in a paper by Mr. Panchanan Das.[1] The astrophysical importance of the Doppler effect in molecular scattering in such cases as for instance, the light of the sun's corona is fairly obvious, and has already been emphasised by Fabry.[2]

Planck's Law and Molecular Scattering.

78. The Doppler effect in molecular diffraction is also of theoretical importance from another standpoint. Consider a space bounded by completely reflecting walls and containing enclosed within it radiant energy corresponding to some known temperature distributed amongst the different wave-lengths according to Planck's law of radiation. We may assume further that the

[1] Bulletin of the Calcutta Mathematical Society, 1921, pp. 6-10.

[2] Journal De Physique, Tome 7, 1919, pp. 89-102.

enclosed space contains a few molecules of a gas at the same temperature, and for simplicity also assume that the molecules do not either absorb or emit light but merely scatter the radiations incident on them in accordance with the Rayleigh law of scattering. Owing to the movement of the molecules, the scattered energy will not always have the same wave-length as the incident waves, and hence the postulated conditions provide a mechanism for the interchange of energy between different wave-lengths. If, further, we assume that the molecules scatter the waves incident on them continuously, the mechanism provided for the interchange of energy would operate according to the classical laws of electrodynamics, and the final distribution of energy in the enclosure would not be that given by Planck's law but would necessarily be that consistent with the principle of the equipartition of energy[1] *viz.*—

$$f(\lambda)\ d\lambda = 8\pi\ \mathrm{RT}\ \lambda^{-4}\ d\lambda$$

In other words, the distribution of energy in the enclosure which was postulated in the first instance would be altered, and the thermodynamic equilibrium of the system would be upset. As the system was assumed to be initially at the same temperature throughout, such a conclusion is *primâ facie* inacceptable, and we must therefore draw the inference either that the Rayleigh law

[1] *Cf.* Jeans; Report on Quantum Theory, § 10.

of scattering is not valid or that the molecules do not scatter the radiations incident on them continuously. Since the Rayleigh law of scattering is supported by experiment, at least over a considerable range of wavelengths, it seems more reasonable to accept the latter conclusion, and to infer that molecular *scattering of light* cannot take place in a continuous manner as contemplated by the classical electrodynamics. It seems to be difficult, however, to reconcile this with the hypothesis that light is propagated through space in the form of continuous waves, and we are apparently forced to consider the idea that light itself may consist of highly concentrated bundles or quanta of energy travelling through space. This will be further discussed in the following chapter.

CHAPTER IX

Molecular Diffraction and the Quantum Theory of Light

79. In the year 1905, Einstein [1] put forward the hypothesis that the energy of a beam of light is not distributed continuously in space but that it consists of a finite number of localised indivisible energy-bundles or "quanta" capable of being absorbed or emitted only as wholes. The theory had some notable successes to its credit, especially the prediction of the photo-electric equation and the explanation of the phenomena of ionisation of gases by X-rays. Nevertheless it has been felt that very serious difficulties stand in the way of its acceptance. Maxwell's electro-magnetic theory conceives the energy of light as distributed in a continuous manner through space and offers a satisfactory explanation of whole groups of phenomena, the mere existence of some of which, especially those classed under the heading of interference and diffraction, seems very difficult to reconcile with the hypothesis of light-quanta. The tendency has therefore been to regard the propagation of light in space as determined by Maxwell's equations, but that

[1] Annalen der Physik, p. 132, 17, 1905.

these equations for some reason or other fail when we have to deal with the emission or absorption of energy from atoms or molecules. The discontinuity is thus conceived to be limited to the act of emission or the act of absorption or of both. Historically, the quantum hypothesis had its origin in the derivation of Planck's radiation formula, and an assumption that the discontinuity occurs only in emission is apparently sufficient for that limited purpose. Hence, though Planck's hypothesis of quantum emission, reinforced as it has been by the success of Bohr's theory of line-spectra, has passed into general acceptance, Einstein's idea of light-quanta has apparently been regarded as unnecessarily revolutionary in character. This feeling has perhaps been strengthened by the considerable degree of success which has attended the use of the "correspondence-principle" recently introduced by Bohr in which an attempt is made to effect a reconciliation, limited though it be, between Maxwell's theory and the quantum theory of emission of light.

80. If, however, we view the matter from a purely philosophic standpoint, Einstein's original conception of the discontinuous nature of light itself has much to recommend it. It fits in with the assumed discontinuous character of the emission and absorption of energy as part of a consistent and homogeneous theory, whereas the idea that

emission and absorption are discontinuous while the propagation of light itself is continuous belongs to the class which Poincaré has described as "hybrid hypotheses." Such hybrid hypotheses may temporarily serve as useful planks to bridge gaps in existing knowledge, but there is little doubt that they must ultimately make way for a more consistent system of thought. Historically, Maxwell's theory is the embodiment of the belief of nineteenth-century physicists in the validity of Newtonian dynamics as applied to physical phenomena in their ultimate analysis, and especially as applied to phenomena occurring in the medium which was postulated as pervading all space. The belief in the validity of Newtonian dynamics as applied to the ultimate particles of matter has however received a rude shock from the success of the quantum theory as applied to the theory of specific heats, and there seems no particular reason why we should necessarily cling to Newtonian dynamics in constructing the mathematical frame-work of field-equations which form the kernel of Maxwell's theory. Rather, to be consistent, it is necessary that the field-equations should be modified so as to introduce the concept of the quantum of action. In other words, the electrical and magnetic circuits should be conceived not as continuously distributed in the field but as discrete units each representing a quantum

of action, and possessing an independent existence, somewhat in the manner of vortex-rings in a perfect fluid. Interference and diffraction phenomena may then be conceived of as arising from the approach or separation, *i.e.*, crinkling of the mean "lines of flow" of energy in the field.

81. Bohr's theory has made the idea familiar that the emission or absorption of light from the atom or the expulsion of an electron involves something in the nature of a catastrophic change in the atom itself. If, therefore, we wish to look for some experimental support for Einstein's conception that light itself consists of quantum units, we must consider those optical phenomena in which obviously no such catastrophic change in the atoms or molecules is involved. The molecular diffraction or scattering of light is obviously such a phenomenon, which stands in the most intimate relationship with the general theory of the propagation, reflexion, refraction and dispersion of light. If we found that the phenomena of molecular scattering of light are completely and satisfactorily explained on the basis of the classical electromagnetic theory, the case against Einstein's conception would be enormously strengthened. If, on the other hand, we find that the classical theory based on the idea of continuous wave-propagation breaks down and fails to explain the observed facts, we should

naturally feel called upon to revise our ideas regarding the nature of light itself.

82. In view of the foregoing remarks, the fact already mentioned in a previous chapter that the scattering power of compressed carbon dioxide gas as determined by the present Lord Rayleigh is far smaller than that which is indicated by the Einstein-Smoluchowski formula appears highly significant. The theoretical formula expresses the scattering power of the medium in terms of its compressibility and refractive index, and is based on the conceptions of the kinetic theory of matter and of Maxwell's electromagnetic theory of light. It expresses the scattering power of a gas at ordinary pressures correctly, and also the scattering power of liquids with tolerable accuracy. But it fails altogether to express the scattering power of compressed carbon dioxide gas under the conditions of Lord Rayleigh's experiments, that is, when it is in the form of a saturated vapour below the critical temperature. There are three possible alternatives in explanation of this failure; firstly that the derivation of the formula is not valid for some reason or another in the particular conditions of Lord Rayleigh's experiment: secondly that the conceptions of the kinetic theory are invalid under those conditions: thirdly that the continuous wave-theory of light does not represent facts.

83. In respect of the alternative explanations referred to in the preceding paragraph, it may be pointed out that the experimentally observed result is precisely what might be expected according to the conception that light consists of discrete quanta moving through space. If we imagine a stream of such quanta passing through a highly compressed gas, scattering of light would result when a quantum encounters a molecule and suffers a large-angle deviation in its path. Such encounters would occur according to the laws of chance; in other words, the molecules should be regarded not as scattering light continuously but only occasionally, and at any instant, only a small proportion of the molecules distributed at random through the gas are in action. Hence the total number of quanta scattered in any appreciable interval of time would be simply proportional to the number of molecules per unit volume, and would be practically independent of the actual manner in which they are distributed in the space, so long as a quantum is regarded as impinging on only one molecule at a time and not on two or more simultaneously. In other words, the principle of additivity of the energies scattered by the individual molecules would be applicable even in the case of a highly compressed gas for which Boyle's law does not apply. This is the result actually obtained, whereas on the continuous

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wave-theory in which all the molecules are conceived of as scattering light all the time, the resultant effect would depend on their distribution in space, and in the case of a highly compressible gas would not be determined by the additive principle. In fact, the observations of Lord Rayleigh were regarded by him as supporting the principle of additivity of the energy-effects of individual molecules, and this principle, as we have seen, cannot be reconciled with the results of the classical wave-theory under the conditions of the experiments.

84. Though, *primâ facie*, the phenomena of molecular scattering in highly compressed gases seem thus to support Einstein's conception of light-quanta, the cautious reader would naturally wish to make sure that the two alternative explanations of the result suggested above must be excluded. So far as can be judged on the available evidence, neither of the two alternatives seems very probable. In order, however, to exclude them definitely, two series of experiments have been undertaken in the author's laboratory at Calcutta. In the first series of experiments which is being carried out by Mr. K. R. Ramanathan, an attempt is being made to confirm Rayleigh's result for the scattering by compressed carbon dioxide and extend it to the case of *unsaturated* vapours and also to gases at temperatures considerably above the critical

temperature. It is hoped to find the scattering power of various gases and vapours besides carbon dioxide over a wide range of pressures and temperatures. If the experiments support Rayleigh's result, the experimental basis for inferring the failure of the Einstein-Smoluchowski formula would be greatly strengthened. In the second series of experiments which has been undertaken by Mr. J. C. Kameswararao, an attempt is being made to study the Brownian movement quantitatively in gases and vapours under high pressures, in order to find whether the energy of molecular movement indicated by the kinetic theory agrees substantially with that found in experiment. The results of the two sets of experiments may well enable a final judgment to be arrived at regarding the validity of Einstein's conception of the propagation of light in quanta.

85. The belief in the correctness of the principles of the wave theory is to a large extent based on the quantitative agreement between the co-efficients of reflexion and refraction indicated by Fresnel's formulæ and those found in experiment. Already certain failures of Fresnel's formulæ are known, as for instance the existence of reflexion at the boundary between two media having equal refractive index,[1] and it seems important to make a

[1] Rayleigh, Scientific Papers, Vol. V.

careful re-investigation of the co-efficients of reflexion and refraction in various cases, *e.g.*, at the boundary between a liquid and its vapour slightly below the critical temperature, in order to find whether the quantitative agreement between the results of the classical wave-theory and the facts is really so brilliant as is generally believed.

86. The phenomena presented by the scattering of the X-rays and especially the well-known failure to obtain any refraction of X-rays will no doubt have to be re-discussed in the light of foregoing remarks and the results of the optical experiments.

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